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NOTES ON THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND H. W. GEROMANOS.

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SOME years ago, 1896, Rolfe and Defren[1] published analytical data of acid-hydrolyzed starch products from which they concluded that the evidence was strong that a constant relation existed between the optical rotation and copper reduction of such products, independent of the conditions of hydrolysis; in other words, that hydrolyzed products of the same rotation had the same reducing power, and consequently were identical in composition, providing, of course, that they were normal, unmixed products of acid hydrolysis. Obviously, absolute confirmation of such a far-reaching law could only be arrived at by elaborate and lengthy research.

In 1897, Brown and Morris[2] published the results of some 500 analyses of *diastase*-converted starch products, showing, in confirmation of their earlier conclusions, that a law of relation did exist, not only in such products themselves, but in their fractions obtained by alcohol.

Perhaps the most important paper, bearing directly on the acid hydrolysis of starch, is that of Johnson, which appeared in 1898.[3]

[1] This Journal, **18**, 869; revised: *Tech. Quart.*, **10**, 133

[2] *J. Chem. Soc.*, **71**, 115.

[3] *Ibid.*, **73**, 490.

Johnson found a constant relation between optical rotation and cupric reduction, but obtained results at variance with those of Rolfe and Defren.

Johnson concluded that maltose, or its molecular combinations, was not found in acid-hydrolyzed products, but that these bodies could be considered to be combinations of dextrose and a non-reducing dextrin, thus agreeing with earlier work, notably that of Salomon[1] and Pellet,[2] who had already come to the same conclusion.

Johnson ascribes the differences shown in Rolfe and Defren's data to errors introduced into the work of the latter through lime salts formed in neutralizing the acidified solutions. He publishes but little of his experimental data or the details of his work, but states that he has followed the analytical procedure of Brown and Morris, and that his conversions were made on a water-bath in open beakers. Apparently the hydrolyzing acid was sulphuric, originally, of about half-normal strength. We understand that Krieger has also published a paper confirming the work of Johnson, but we have not been able to find reference to it.

Morris[3] stated that the results of his investigations were quite at variance with those of Johnson; that his data indicated the presence of maltose, which he proved to exist in the solutions by obtaining crystals of undoubted maltosazone; furthermore, his results confirmed those of Rolfe and Defren, although he was inclined to doubt the universal application of their law of relation to all acid-hydrolyzed starch products. The untimely death of this brilliant investigator has doubtless prevented publication of his complete work.

Many circumstances have prevented the resumption of these investigations in this laboratory. Only quite recently has this research been taken up again with the following objects: (1) To obtain more data on the "law of relation"; (2) to see whether this law applied to alcoholic fractions; (3) to find out proofs of the existence of maltose in acid-hydrolyzed starch products.

The methods of the English chemists, adopted by us, have been much criticized, owing to the use of an arbitrary specific gravity factor in the calculations. As the use of this factor, its influence

[1] *J. prakt. Chem.* (2), **28**, 82.
[2] *Compt. Rend.*, **2**, 450.
[3] *Proc. Brit. Assoc.*, Sept., 1899.

on the results, and their relation to the absolute values, etc., have been fully explained by Brown and Morris,[1] it is not necessary to discuss it in detail here. In the present work we have expressed the results in absolute values. It should be noted, however, that the use of the factor 0.00386, as detailed by Brown and Morris, simplifies the calculations, gives correct *proportional* values (per cents.) of the primary carbohydrates, and likewise optical and reducing figures, readily convertible into absolute values by use of known factors. The practical starch chemist, therefore, will probably continue the use of it, as a path of least resistance in attaining his desired information, just as the analyst will use the Mohr cubic centimeter, and the physical chemist the Briggs logarithm instead of the Naperian, when by such means he arrives at his objective point more quickly and easily. Results obtained by such expedients of calculation and experiment are permanently valuable, as they admit of standardization at will in terms of the accepted scientific constants of the day.

Analytical Methods.—In the earlier work, densities were obtained by a Westphal balance, carefully and frequently adjusted, and were made at ordinary laboratory temperatures, and corrected for 15.5°. More recently, we have made pyknometer determinations at 15.5°. Corrections were made for the dissolved mineral salts present. Ash determinations of carbohydrate solutions containing known amounts of mineral salts confirmed O'Sullivan's factor, 0.008, for the density correction of each gram of mineral matter, determined as ash, in 100 cc. of solution, when the amount of mineral matter did not exceed a few per cent. of the carbohydrate present. A more exact correction seems necessary when the mineral content is large. Ash determinations were made in a "low temperature" muffle, vaseline being used to prevent excessive swelling of the coal.

This influence of the mineral salts in solution was investigated with particular care, owing to its possible importance as a source of error, as suggested by Johnson. Evidently the most important error introduced, that of the density, lowers the cupric-reducing power and optical rotation by the same percentage, the error in reduction appearing greater in the higher converted products, that of the rotation in the lower. Hence, the effect of the ash correction on the reduction values of those products containing

[1] *J. Chem. Soc.*, **71**, 72.

the most sugars would be diametrically opposite to that suggested by Johnson's criticism. As a matter of fact, the correction for the concentration of acid used rarely exceeds 2 per cent., and in the majority of cases is much smaller. This would tend to increase the discrepancy of more than 10 per cent. between Johnson's and Rolfe and Defren's figures in those products where the presence of maltose is in dispute; that is, at the conversion point where maltose is supposed to be present in maximum amount.

We have made a careful study also of the original data of this earlier work and have recalculated all the results where the data admitted. This was made necessary from the revision of factors used in calculation. We have tabulated all these values figured in absolute constants. It will be seen that little change is made, many of the corrections being compensatory.

Another possible source of error caused by lime salts might be their precipitation with the copper oxide in the Fehling test. This seemed improbable, as the mineral matter rarely exceeded 0.100 gram in 100 cc. in the original solutions, which were diluted in most cases to $^1/_{80}$ of their original concentration. Blank tests made on solutions containing lime salts in the proportion present in the usual tests, and in fact, made by neutralizing an acidified solution in the same manner as the hydrolyzed products, showed no increase in weight due to precipitated lime.

The optical rotation constants have been determined by a Schmidt and Haensch saccharimeter, but the light factor used in converting readings to angular degrees of rotation of the "D" ray has been increased 0.2 per cent. to 0.3450. The original factor, 0.3443, which was worked out experimentally,[1] expresses the value of our saccharimeter in terms of yellow-light rotation, measured on a Laurent polariscope, the light being that of a sodium chloride flame, filtered through a section of potassium bichromate crystal. The Landolt polariscope uses sodium chloride, light filtered through a potassium bichromate solution, and also one of uranium sulphate. This seems to have caused a change in light standard which results in readings which are 0.2 per cent. higher. The wave length of the Landolt illuminating apparatus has been found to be 0.00058932,[2] corresponding to a position in the spectrum exactly midway between the two "D" lines. As the

[1] This Journal, **18**, 873.

[2] Landolt's "Das Optische Drehungsvermögen," p. 264.

Landolt values seem to be generally accepted as the standard for the "D" ray, we have made this trifling change in our own figures. The subject of the "light factor," that is, the equivalent value of one saccharimetric division in angular degrees of yellow-light rotation, is treated by recent text-books in a misleading way. Values are given some tenths of a per cent. higher than those of the earlier works, leading the reader to infer that the earlier figures are incorrect, whereas, as a matter of fact, these earlier factors are practically exact for by far the majority of saccharimeters in actual use to-day—those graduated in "Mohr" cubic centimeters at 17.5°, the only correction being for any change in the light standard of the rather indefinite "D" ray. The recent factors are obviously applicable only to those instruments recently made which are graduated for solutions made up in true cubic centimeters. Unquestionably, the use of volumetric apparatus graduated in true cubic centimeters is most commendable, but just as unquestionably, the starch chemist must use those factors which are applicable to the actual graduation of his saccharimeter. It is to be hoped that the makers of saccharimeters henceforth will mark on the instruments just how they are graduated.

As far as possible, saccharimeter readings have been made at 20° C., but, with the present laboratory facilities at our command, it has been impossible to control the temperature within several degrees. As soon as it is feasible to carry out such work, we intend to make a correction table for readings taken at temperatures other than 20°. Our determinations of cupric-reducing power have been made by Defren's method,[1] with slight modification. We have preferred this method to that of Brown and Morris,[2] which it closely resembles, merely because we obviate the correction due to the spontaneous reduction of the solution. In the past six years we have made blank tests on every lot of Fehling solution used, carrying out every detail of the regular determination. With the exception of two lots of solution—in which we traced the spontaneous reduction of 0.0017 gram to a bottle of Rochelle salts of inferior quality—we have never found either visible evidence of spontaneous reduction, or increase in weight of crucibles, these checking within 0.0002 gram. Therefore, we state with confidence that there is no spontaneous reduction of

[1] This Journal, **18**, 749.

[2] *J. Chem. Soc.*, (London), **71**, 94.

the Fehling solution during the heating process of the test carried out by Defren's method. This seems to be the result of the greater dilution of the Fehling solution, and possibly the smaller amount of alkali. We have varied the method, however, in one detail. Instead of delivering the sugar solution as quickly as possible from a burette into the Erlenmeyer flask containing the hot, diluted Fehling solution, we have added the sugar all at once, without removing the Fehling liquor from the bath, by quickly inverting a 25 cc. flask which is left upside down in the mouth of the Erlenmeyer during the reduction. One short rotary shake is given the Erlenmeyer immediately after the solution is added to insure, at once, perfect mixture. This modification has increased the reducing power of the sugar solutions, and necessitated calculating a new set of equivalents, from tests made with pure dextrose. As we hope to modify the process somewhat more in the near future, we do not deem it advisable to take valuable space to publish our present equivalent table. The copper reduction, in general, both on dextrose and maltose, is about 5 per cent. greater than Defren's original figures, the dextrose equivalent, therefore, being correspondingly less. In the earlier work some correction has been necessary, owing to the more accurate density values for dextrose and maltose, which are now known.[1] These density corrections lower Defren's original equivalents about 0.6 per cent. and need only be considered in the most accurate work.

As the density factors corresponding to the actual weights of acid-hydrolyzed starch products, in solutions of a density approximating 1.04, have already been established experimentally,[2] we have been enabled to convert our results into absolute values by the following table (A), which gives the logarithms for convert-

TABLE A.—DENSITY FACTORS FOR REFERENCE TO ACTUAL WEIGHTS OF ACID-HYDROLYZED STARCH PRODUCTS IN 100 TRUE CUBIC CENTIMETERS OF SOLUTIONS.

$[\alpha]_{D}^{20°}$	Density factors $\left(d\frac{15.5°}{15.5°}\right)$.	Logarithms of conversion factors.[3]
55°	0.003837	9.9965
60°	0.003844	9.9973
65°	0.003850	9.9980
70°	0.003857	9.9988
75°	0.003864	9.9996
80°	0.003870	0.0002

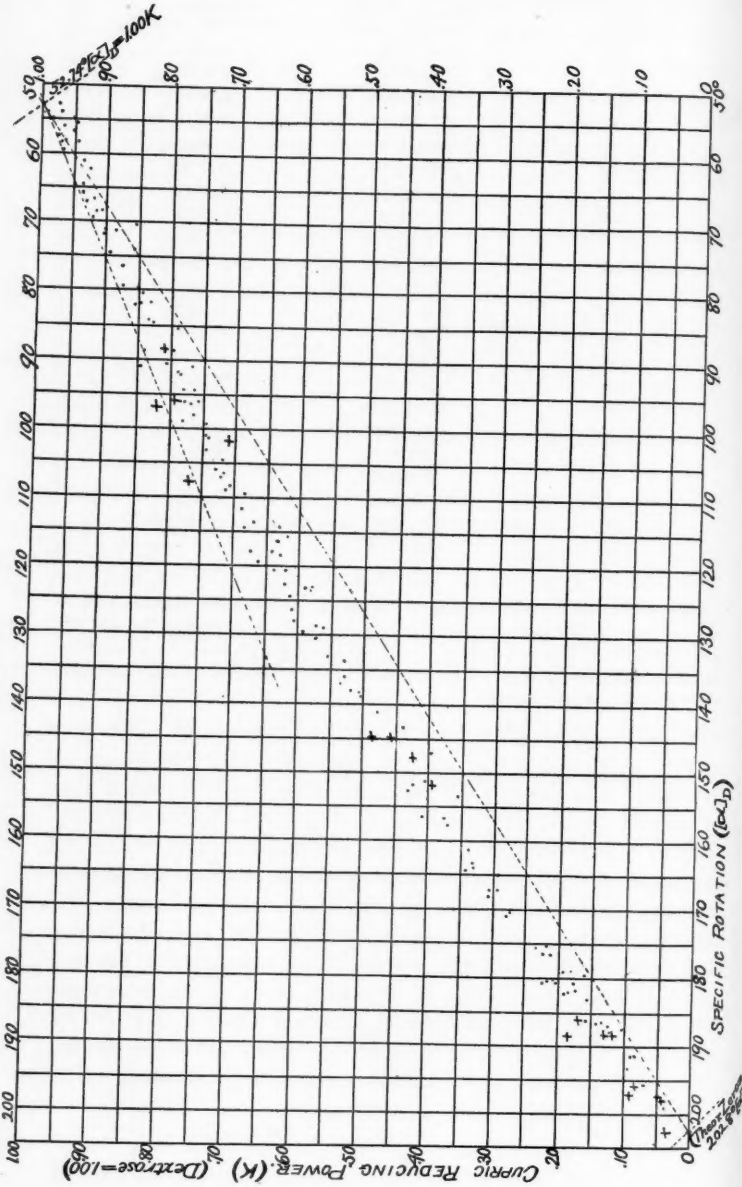
[1] *J. Chem. Soc.* (London), **71**, 79.
[2] This Journal, **19**, 698.
[3] Log. $\frac{F}{0.00386}$ 0.99802.

$[\alpha]_{388}$.	Density factors $\left(\frac{d\ 15.50}{15.50}\right)$	Logarithms of conversion factors.[1]
85°	0.003877	0.0010
90°	0.003884	0.0018
95°	0.003890	0.0024
100°	0.003897	0.0032
105°	0.003904	0.0040
110°	0.003911	0.0048
115°	0.003918	0.0056
120°	0.003925	0.0063
125°	0.003931	0.0070
130°	0.003938	0.0078
135°	0.003945	0.0085
140°	0.003951	0.0092
145°	0.003958	0.0100
150°	0.003965	0.0107
155°	0.003971	0.0114
160°	0.003978	0.0121
165°	0.003985	0.0129
170°	0.003991	0.0136
175°	0.003998	0.0144
180°	0.004005	0.0151
185°	0.004011	0.0157
190°	0.004017	0.0164
195°	0.004023	0.0170

NOTE.—As the cupric-reducing power of pure dextrose, taken as 1.00 for the factor 0.00386 is 0.9915 in absolute value, it is necessary to add the co-logarithm of this number, or 0.0037, to the logarithm of the conversion factor in calculating the reducing power in terms of that of the equivalent weight of dextrose as unity.

ing results calculated by the factor, 386, into values referred to grams of hydrolyzed product in 100 true cubic centimeters of solution. The newer work published in this paper covers a comparatively limited field, being an investigation of hydrolyzed products of several commercial starches of different origin, formed by the action of hydrochloric acid at two concentrations, and at pressures between 2 and 3 atmospheres, unless otherwise stated. No attempt has been made to purify these starches, as we have been led to believe not only that purification is unnecessary, but may actually change the nature of the starch, since, in our experience, all purification methods produce a certain amount of hydrolytic change and formation of products which are diffusible through the starch grains, and subsequently removed by washing. That

[1] Log. $\frac{F}{0.00386}$ 0.99802


CUPRIC REDUCING POWER (K) (Dextrose=100)
SPECIFIC ROTATION ([α]D)

such diffusion actually does take place, can be proved by testing the wash-waters used in the purification of starch with iodine, or shaking up the starch itself with cold water and testing the water. The colors obtained are not the deep blue of the unchanged and indiffusible starch, but the violet of hydrolyzed starch, providing, of course, that the grains are unruptured. Probably this slight loss from hydrolytic change has no influence on the results, when the purification method is not too drastic, but it is questionable whether the "purified" product obtained is any nearer pure *starch* than the original.

The following table (B) gives the corrected values of Rolfe and Defren's original work, together with those recently obtained by us. The plotted results[1] make it clear that the reducing values do not lie on a straight line as they should, if dextrose alone were present. On the contrary, the results are in substantial agree-

TABLE B.

Starch.	Acid.	Concentration.	$[\alpha]_D$.	κ.
Corn	HCl	N/100	147.0	0.489
			100.9	0.750
			73.8	0.855
			199.2	0.043
			179.6	0.161
			156.6	0.375
			129.2	0.563
			149.2	0.451
			88.8	0.799
			65.6	0.937
			58.2	0.974
			53.6	0.977
			180.5	0.206
			133.4	0.555
			108.7	0.712
			68.1	0.921
			59.0	0.949
			151.4	0.403
			118.0	6.637
			90.8	0.768
			70.3	0.855
			61.8	0.933
			164.4	0.346
			135.9	0.529
			92.4	0.786
			168.5	0.305

[1] The plotted values marked by a cross are those of alcoholic fractions, to be discussed in a subsequent paper.

Starch.	Acid.	Concentration.	$[\alpha]_D$.	κ.
			141.7	0.510
			126.3	0.610
			101.2	0.745
Corn	HCl	N/200	195.6	0.067
			186.3	0.143
			180.6	0.225
			167.3	0.306
			160.3	0.349
Corn	HCl	N/100	108.1	0.705
			94.4	0.778
			81.9	0.854
			76.3	0.877
			187.7	0.122
			159.9	0.382
			120.5	0.640
			74.5	0.899
			71.1	0.902
Corn	$H_2C_2O_4$	N/100	181.8	0.172
			160.1	0.360
			138.7	0.504
Corn	$H_2C_2O_4$	N/50	140.9	0.485
			134.0	0.529
			120.4	0.623
			58.1	0.970
			136.9	0.538
			87.1	0.896
Corn	HCl	N/100	182.3	0.192
			186.9	0.128
			193.3	0.097
			186.0	0.158
			182.0	0.186
			180.3	0.217
			167.2	0.298
Potato	HCl	N/50	164.9	0.296
			153.9	0.358
			143.5	0.444
			144.9	0.457
			137.6	0.523
			127.8	0.604
			119.6	0.660
			163.9	0.333
			124.6	0.614
			116.2	0.639
			111.5	0.694
			103.2	0.750
Corn	HCl	N/50	130.4	0.574
			125.5	0.617

Starch.	Acid.	Concentration.	$[\alpha]_D$.	K.
			117.7	0.645
			114.2	0.673
			107.3	0.723
Corn	HCl	N/50	109.7	0.680
			104.7	0.722
			99.3	0.750
			95.9	0.760
			91.9	0.790
			90.4	0.808
Cassava	HCl	N/50	79.8	0.852
			78.6	0.875
			74.0	0.884
			71.7	0.903
			96.2	0.773
			90.6	0.850
			84.3	0.835
"Thin boiling" corn-starch	HCl	N/50	81.8	0.851
			66.7	0.933
			60.8	0.941
			59.5	0.973
			57.5	0.980
			122.5	0.623
			114.6	0.631
			106.5	0.720
			97.6	0.769
			179.2	0.195
			52.5	100.4
Corn	HCl	N/50	68.1	0.910
			59.9	0.977
			56.7	0.953
Corn	$H_2C_2O_4$	N/25	163.6	0.333
			129.0	0.569
			98.9	0.783
			80.1	0.849
			69.3	0.925
Corn	H_2SO_4	N/50	170.9	0.281
			130.0	0.562
			105.9	0.728
			84.8	0.832
			71.3	0.889
Corn	HCl	N/100	152.6	0.427
			95.7	0.788
			66.5	0.924
			54.8	0.954
			54.2	0.998
Corn	HCl	N/50	95.8	0.783
			64.6	0.939

Starch.	Acid.	Concentration.	$[\alpha]_D$.	κ.
			55.5	0.972
			52.9	0.979
			88.7	0.843
			55.3	0.951
Corn	HCl	N/25	157.5	0.372
			114.7	0.686
Corn	HCl	N/50	82.0	0.886
			54.9	0.993
Potato	HCl	N/50	175.5	0.234
			151.3	0.404
			180.1	0.208
			156.6	0.406
			191.3	0.094
			176.8	0.213
			158.8	0.331
			123.2	0.592
			123.0	0.583
Cassava	HCl	N/50	151.6	0.427
			182.2	0.184
			118.5	0.668
			183.4	0.157
			94.6	0.783
			85.1	0.795
Potato	HCl	N/50	187.3	0.104
			175.3	0.220
			161.1	0.340
			191.2	0.087
			186.1	0.135
			180.7	0.176
			176.7	0.221
			170.4	0.275

ment with the original ones of Rolfe and Defren. While the tabulated values of the original paper, calculated on the factor 0.00386, are not exact, they have proved to be sufficiently approximate to be valuable aids in predicting practical laboratory results. It is intended to use more refined methods of analysis, if possible, and to locate this curve more definitely by the method of least squares. We have published the present figures, however, as conclusive of the presence of another reducing body than dextrose in acid-hydrolyzed starch products, formed under the conditions of conversion which we have defined.

SUGAR LABORATORY, MASS. INST.
OF TECHNOLOGY.

THE PRESENCE OF MALTOSE IN ACID-HYDROLYZED STARCH PRODUCTS.

By Geo. W. Rolfe and Isaac T. Haddock.

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References have already been made, in a previous paper,[1] to the works of Salomon, Pellet, Johnson, and others which have led these investigators to conclude that maltose is not a product of the acid hydrolysis of starch. Lintner and Düll believed that "isomaltos" was produced. Morris and Rolfe and Defren have been among those who have maitained that maltose resulted from the hydrolysis. As has already been cited in a previous paper, Morris has stated that he has made crystals of undoubted maltosazone from the products of acid-hydrolyzed starch.

Having at hand a large quantity of commercial "glucose," of which we knew the circumstances of manufacture—it being the product of hydrochloric acid hydrolysis at a pressure of two atmospheres, and having a specific rotation of 126.5° D, and a cupric-reducing power of 0.575—we decided to make alcoholic fractions of this glucose with the object of separating maltose, if present, or some of its compounds, and, incidentally, of testing the law of relation of rotation to cupric reduction as applied to alcoholic fractions. The analytical figures of this sample showed that the hydrolysis had been carried only a little beyond the point for maximum maltose content as calculated from Rolfe and Defren's tables, and, in consequence, was specially suited for the investigation.

It can be easily calculated from the same tables that, were it possible to remove all the dextrin from a solution of this glucose leaving all of the maltose and dextrose, the resulting product would have a rotation of 105° and a reducing power of 0.76. If, however, the fractionation separated the glucose into a series of products more or less soluble in alcohol, but containing all three of the primary carbohydrates, it would be probable that they would conform to the law of relation, in which case, should a product be separated of the rotation 105°, its cupric-reducing power would be about 0.71 instead of 0.76.

In carrying out the fractioning, a 15 per cent. solution of glu-

[1] Preceding paper.

[2] *Ber. d. chem. Ges.*, **28**, 1522.

cose was added, drop by drop, to about ten times its volume of 95 per cent. alcohol. After standing for a day or more, the precipitate was filtered off, washed thoroughly with alcohol, dried at a gentle heat till all traces of alcohol were expelled, and tested in the usual way. In the case of the alcoholic filtrates, the alcohol was removed by distillation, and the residues were concentrated to about 10 per cent. In order to economize time and alcohol, a little fuller's earth was mixed with the first precipitates to facilitate separation.

The following table gives the optical and reducing constants of those fractions which were investigated. It will be seen that, in general, they show a relationship between optical rotation and copper-reducing values which is in practical agreement with that found for homogenous acid-hydrolyzed products.

ALCOHOLIC FRACTIONS OF COMMERCIAL GLUCOSE SOLUTIONS.

		$[\alpha]_D$.	κ.
1st.	*Fractionation:*		
	1st. Precipitate	145.2°	0.489
	2nd. "	149.0°	0.423
	3rd. "	198.0°	0.047
	4th. "	197.6°	0.051
	1st. Filtrate	107.9°	0.765
	2nd. "	101.6°	0.717
	3rd. "	98.3°	....
	4th. "	96.8°	0.815
2nd.	*Fractionation:*		
	2nd. Precipitate	188.0°	0.117
	3rd. "	197.2°	0.093
	4th. "	196.0°	0.085
	2nd. Filtrate	88.8°	....
	4th. "	88.1°	0.811
3rd.	*Fractionation:*		
	1st. Precipitate	154.6°	....
	2nd. "	168.1°	....
	3rd. "	185.7°	0.163
	2nd. Filtrate	84.4°	....
4th.	*Fractionation:*		
	1st. Precipitate	137.5°	....
	2nd. "	152.3°	0.395
	3rd. "	165.9°	....
	4th. "	187.9°	0.127
	5th. "	189.1°	0.189
	6th. "	194.3°	0.075
	1st. Filtrate	96.0°	0.792

The values for the cupric-reducing powers of the filtrates of the first fractionation all show a wide departure from such relationship. These filtrates were peculiar in that they deposited, to some extent, granular precipitates quite different in appearance from the separated dextrins. It seemed probable that this precipitate was sugar in a free state. Moreover, it seems more than a coincidence accounted for by experimental error that the plots of these reducing values almost exactly fall on a straight line joining the 100 and 62.2 points which theoretically defines the reducing values of mixtures of pure maltose and dextrose. The apparently low reducing power of the second filtrate may be caused by an error in the rotation reading, as the aqueous solution in this case was turbid. This evidence seems to point to the possibility that under certain conditions, not clearly defined, alcoholic fractionation may break up the hydrolytic products, setting free one or more of the primary carbohydrates.

Some of the precipitates, especially those of high rotation, show unexpectedly high cupric-reducing powers. We are inclined to believe that this is caused by partial hydrolysis during drying. The precaution of drying in a vacuum at low temperature may not have prevented this entirely, as these low-converted dextrins seem very sensitive in this respect.

An aqueous solution made from the second filtrate of the third fractionation was heated on a water-bath with a small quantity of a solution of phenylhydrazine, in glacial acetic acid. Maltosazone was separated in the usual way by filtering off the dextrosazone in a hot funnel. On cooling the filtrate, characteristic crystals of maltosazone separated out. The dried crystals, tested by heating in a capillary tube, attached to a thermometer bulb, and immersed in a sulphuric acid bath, according to the usual method, began to decompose at about 195°, being entirely melted at 203°. The ordinary basic lead acetate solution of a density of 1.25, such as is commonly used in sugar analysis, proved very convenient for separating maltose. This solution was not precipitated when dropped into pure 95 per cent. alcohol, but formed a white, curdy precipitate when poured into the alcoholic filtrate from the glucose fractionation. After the lead was completely removed by hydrogen sulphide, the aqueous solution was heated with phenylhydrazine. No precipitate formed in the hot solution,

but maltosazone separated out on cooling. As this seems a promising means of separating maltose, we intend to investigate it further.

We have made some photo-microscopic studies of the maltosazone and dextrosazone obtained from the alcoholic fractions and by means of the lead acetate separation, comparing them with corresponding osazones obtained from pure maltose and dextrose. When pure maltose is treated with phenylhydrazine acetate in the usual way, the osazone often separates out in crystal plates large enough to be seen without magnification. If examined under the microscope, it will be noticed that these plates tend to collect in spherical masses. Plate I shows such crystals of the osazone made from Kahlbaum's C. P. maltose. We have found it impossible to obtain these large crystals by recrystallization from hot water, the osazone being deposited in small balls[1] which show, on close examination, that they are aggregates of flat crystals. Plate II, while a poor photograph, is interesting because it represents these balls obtained from the crystals shown in the first plate by recrystallization from hot water. Plate III shows crystals of maltosazone obtained from the alcoholic filtrate previously mentioned. This shows the plates in loose aggregations and in balls. Plate IV is of osazone crystals from the lead acetate precipitate of the same filtrate. Plate V shows the same crystals after the aggregates have been broken up by gentle tapping of the cover-glass.

Dextrosazone has a quite different crystal habit. The crystals can be described as needles rather than plates. They form brush-like bundles resembling tufts of broom-corn, which, to some degree, suggest the maltosazone aggregations, but yet are quite different, showing none of the compact, spherical forms so characteristic of maltosazone. More highly magnified dextrosazone crystals closely resemble in shape those of stibnite, and apparently belong to the orthorhombic or hexagonal system. Plate VI shows these characteristics, especially the square basal angles. We have found these crystal forms so characteristic, when studied with the microscope, that we have felt warranted in presenting these photo-micrographs, and would have illustrated further the osazones of these two sugars had space permitted. The crystalline structure and the behavior of the two osazones with hot water

[1] Grimbert: *J. Pharm. Chim.*, 7-17-5, aptly terms them "rosettes."

Plate I.

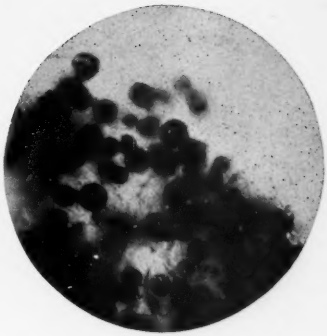

Plate II.

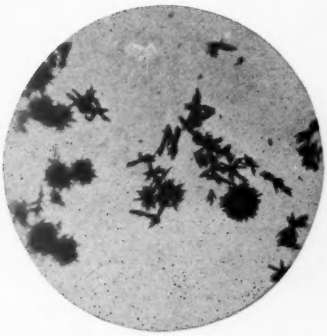

Plate III.

Plate IV.

Plate V.

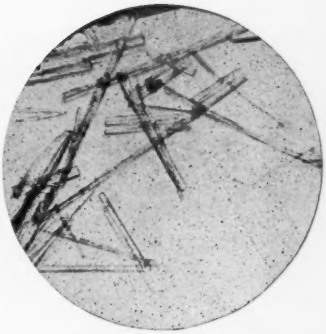

Plate VI.

are, in our opinion, their most easily recognized distinctions. The melting-point test by itself, as already pointed out by Brown, Morris and Miller,[1] is unreliable, and has led to serious errors of identification. This is due to the slight differences in the values in the case of many of the sugars, the difficulty in getting the exact melting-points owing to decomposition, and the great influence of very small amounts of impurities difficult to remove.

SUGAR LABORATORY, MASS. INST.
OF TECHNOLOGY.

A STUDY IN RAFFINOSE DETERMINATIONS.

BY DAVID L. DAVOLL, JR.

Received July 23, 1903.

THE existence of several methods for the determination of raffinose in the presence of saccharose, together with variable results obtained in the application of the same to the analysis of the same product, have impelled me to investigate the matter more closely after the close of the "campaign." As the result of a study of the various methods, I have been led to combine the best features of some of them and believe that I have succeeded in applying a slight modification to the method of Clerget, which will secure for it accurate and satisfactory results with dark-colored products. The modification proposed is that of applying powdered zinc after inversion and at the temperature of inversion, with the production of an almost colorless solution with no change in the products of the hydrolysis of either sucrose or raffinose.

As the basis of these experiments a pure, doubly refined, white sugar, of undoubted cane origin, was employed and a commercial sample of raffinose from the house of Kahlbaum. The cane-sugar was perfectly free from invert-sugar and polarized 99.97 per cent. pure after being powdered and dried at a temperature of 60°-70° C.

The one sample of molasses was employed throughout the work.

Three samples of animal charcoal were purchased from a reliable Chicago firm and in original packages as bottled by the German firms of Merck and Dr. König. These chars were dried to constant weight before use at a temperature between 115° and

[1] *J. Chem. Soc.* (London), **67**, 709: "The Isomaltose of C. J. Lintner."

125° C. It is important to know that the moisture content of these chars varied from 7.17 per cent. to 25.7 per cent.

The modern double-field S. and H. instrument employed was very recently checked by means of a quartz plate kindly loaned by the Division of Chemistry, U. S. Dept. of Agriculture, Washington, D. C., and all important points on the scale verified by a pure sugar standardized against the quartz of 90 per cent. polarization. The levo-rotation, when checked against the dextro-rotation, gave the same figure in every instance. The flasks used were all restandardized to hold 100 Mohr cc. All polarizations, both direct and invert, were made in the same jacketed 200 mm. tube and at the standard temperatures of 17.5° C. (for direct) and 20° C. (for inverted) so as to avoid all corrections for variation in specific rotation. The readings as given are averages of at least five separate rereadings.

Some work by G. Reinhardt,[1] calling attention to the often increased levo-rotation where char is used for decolorizing "rest" molasses arising from strontium juices, has impelled me to apply the samples of char mentioned for the purpose of reviewing his findings. Reinhardt mentions that bone-black has been regarded, up to the present time, as diminishing levo-rotation by absorption, while blood-char, in spite of its superior decolorizing power, had to be given up because of high absorption.

Following are our results in determining the effect of char upon a solution of pure cane-sugar after hydrolysis by the strict method of Clerget.

	Original polarization.	Calculated normal basis.
(1) Carbo Sanguinis, acido depur. pro analyse. Dr. König.....	—16.41	—32.82
(2) Animal charcoal, Merck, highest purity, dry	—16.29	—32.58
(3) Animal charcoal, Merck, reagent.	—16.21	—32.42

I have not found the levo-rotation diminished by Carbo Sanguinis, but rather slightly increased. Three grams of all chars were used and the vigorous shaking continued five minutes, with three minutes allowed for filtration. Reinhardt found slight diminution, increasing with blood char.

[1] G. Reinhardt, 1902: "Ueber Raffinosebestimmungen," *Ztschr. d. Ver. für d. Rübenzuckerind. d. deutsch. Reiches*, **2**, 114.

Dr. G. Wiske[1] has elaborated Reinhardt's investigation, working also with dextrose, levulose and galactose in their separate behavior toward chars. Differing with Reinhardt, he finds absolutely no absorption or change when char is applied five minutes to inverted pure sucrose. He explains this invariability by showing in a test with equivalent quantities of levulose and dextrose that the notable absorption of dextrose, together with small absorption of levulose, mutually counteract any error. Where raffinose is present the results are different.

Reinhardt has shown that with rising raffinose content there is increased levo-rotation. In the case of bright after-products having 2.5 per cent. raffinose and using 3 grams of "Klaerkohle" he found the same levo-rotation. He explains this by saying that the absorptive power which diminishes the levo-rotation in the case of inverted pure saccharose is compensated by the simultaneous increase in levo-rotation of inverted raffinose; also due to absorption; hence, where 2.5 per cent. raffinose is present the results are correct, while with less than 2.5 per cent. too little saccharose and too much raffinose is found, though the error is small, while with more than 2.5 per cent. raffinose, too much saccharose and too little raffinose is found. Reinhardt further considers that high levo-rotation is due to absorption of dextro-rotatory melibiose, but he awaits further investigation.

Wiske has also imitated a mixture of raffinose and saccharose by inverting and polarizing a mixture of saccharose, levulose and melibiose, finding a very strong increase in levo-rotation with use of char. In experiments upon mixtures of saccharose and raffinose as they occur in after-product massecuites, sugars and "rest" molasses, he finds the degree of absorption to be entirely dependent upon the quantity of raffinose and indifferent to the quantity of saccharose. Employing half-normal and 3 grams char, he recommends a subtractive correction of $^1/_{10}$ degree for every per cent. of raffinose above 2 per cent.

To ascertain the comparative effect of the three varieties of char upon hydrolyzed mixtures of pure cane-sugar and raffinose, 12.367 grams cane-sugar and 0.657 gram raffinose were hydrolyzed in 75 cc. dilution, according to the strict Clerget method, shaking five minutes with 3 grams char and filtering two to three

[1] G. Wiske, 1902: "Ueber Raffinosebestimmungen," *Ztschr. d. Ver. für d. Ruebenzucker-ind. d. deutschen Reiches.*

minutes. The direct polarization of a normal solution of such a mixture was 102.48 per cent.

	Original polarization.	Calculated normal.	Raffinose.	Sucrose.
Polarization without char.....	—13.50	—27.00	4.16	94.77
(1) Carbo Sanguinis, acido depur. pro analyse. Dr. König	—13.57	—27.14	4.11	94.87
(2) Animal charcoal, Merck, highest purity, dry	—13.70	—27.40	3.95	95.16
(3) Animal charcoal, Merck, reagent	—14.00	—28.00	3.56	95.89

The samples of blood-char, under the conditions, produced a levo-rotation that results in a raffinose content not far removed from polarization without char, which may be explained by the absorption of dextro- and levo-rotatory substances, mutually offsetting each other.

A notable increase in levo-rotation will be shown later in further comparative tests.

The effect of time as a factor in decolorizing, is shown where Merck's highest purity char is used upon the molasses:

	Time of char digestion. Minutes.	Filtration. Minutes.	Original polarization.	Calculated normal.	Raffinose.	Sucrose.
(1).....	5	7	—5.48	—10.96	3.58	43.97
(2).....	10	9	—5.51	—11.02	3.54	44.04
(3).....	15	9	—5.55	—11.10	3.49	44.13
(4).. Decoloration by zinc			—5.48	—10.96	3.58	43.97

The decoloration after fifteen minutes, while slightly more than that of five minutes, was not worthy of consideration. The result in (4) is that obtained by the action of 1 gram powdered zinc for three to four minutes at 69° C. after completion of inversion by the strict method of Clerget and is the modification I would propose as a solution of the vexatious problem of bleaching. It is added here for the sake of comparison and will be referred to later. The direct polarization of this molasses was 50.6 per cent., using lead *-b-* acetate as a precipitant, with and without acetic acidulation, producing identical results in polarization.

The method of Lindet as modified by Courtonne was examined, but gave such widely varying resuts with a mixture of pure cane-sugar and raffinose that the results obtained upon a low product, like molasses, may be credited with difficulty. The method is as follows: 20 cc. of a solution containing $^1/_5$ normal of the substance is placed in a 50 cc. flask, and 5 grams of zinc dust, accurately weighed, are placed in the flask. Heat the flask and con-

tents by immersing in boiling water. Add 10 cc. of dilute hydrochloric acid in portions of about 2 cc. at a time and as frequently as convenient. Prepare the dilute acid by adding to pure hydrochloric acid (sp. gr. 1.2) an equal volume of distilled water. Heat a few minutes after the last addition of acid. The undecomposed zinc occupies a volume of 0.5 cc.; hence, the normal invert reading is obtained by multiplying by 2.475. After the inversion is completed, cool the solution, either quickly or slowly, by setting aside. Complete the volume at 20° C. Mix, filter and polarize at 20° C.

In his original article, Lindet directs that 5 cc. concentrated hydrochloric acid be gradually added in 4 or 5 parts at intervals of five minutes, and that the zinc be filtered off before dilution to 50 cc. A formula is given for use with the Laurent instrument. Spencer[1] gives a formula for use with the S. and H. instrument as follows:

$$(1)\ \text{Sucrose} = \frac{C - 0.493\,A}{0.827} \qquad (2)\ \text{Raffinose} = \frac{A - \text{Sucrose}}{1.85}$$

where A = the direct reading, and C = algebraic sum of direct and invert reading.

For convenience, all calculations based upon formulas (1) and (2) will be designated "Lindet" merely to distinguish them from Herzfeld's.

Results obtained by the Lindet-Courtonne method upon a mixture consisting of 4.9468 grams cane-sugar and 0.2628 gram raffinose (total = $^1/_5$ normal) in 20 cc. distilled water, were as follows:

Original invert reading.	Result on normal.	Raffinose. (Lindet.)	Raffinose. (Herzfeld.)	Saccharose. (Lindet.)	Saccharose. (Herzfeld)	
−10.07	−25.18	4.97	5.33	93.28	92.60	2 cc. dilute hydrochloric acid added every four to five minutes and heated five minutes additional; zinc filtered out.
−9.25	−22.89	6.47	6.81	90.51	89.87	The above repeated, but the zinc *not* filtered out.
−7.00	−17.32	10.05	10.40	83.89	83.23	Whole 10 cc. hydrochloric acid added within three minutes, and heat applied twenty minutes in all; zinc *not* filtered out.
Result by Clerget method		3.78	4.16	95.48	94.77	(For purpose of comparison.)

[1] Spencer: "Handbook for Chemists of Beet-Sugar Houses and Seed-Culture Farms," 1897.

These results show that the method is totally unreliable with products of the above composition.

The Lindet-Courtonne method was then applied to the molasses having a direct polarization of 50.6 per cent. and which by Clerget's method, using 3 grams char and shaking five minutes, gave 3.58 per cent. raffinose and by the decolorization with 1 gram zinc, as is proposed, also 3.58 per cent. raffinose.

Original invert reading.	Result on normal.	Raffinose. (Lindet.)	Raffinose. (Herzfeld.)	Saccharose. (Lindet.)	Saccharose. (Herzfeld.)	
—4.18	—10.45	3.76	3.91	43.65	43.36	Adding hydrochloric acid every five minutes; total heating, twenty-five minutes; cooling quickly and filtering out zinc.
—4.35	—10.77	3.55	3.70	44.04	43.74	Adding hydrochloric acid every four minutes; total heating, twenty-one minutes; cooling quickly zinc *not* filtered out.

The inversion even on "rest" molasses varies with varying conditions of time, etc. The results, besides varying beyond limits of error among themselves, vary also from the results obtained by the standard method, as shown above, where chars are compared upon molasses.

Perhaps the most instructive result is that shown in the following experiment, where are compared: (1) The strict Clerget method without char; (2) the strict Clerget method with 3 grams of Merck's highest purity char after five minutes' shaking; (3) the Lindet-Courtonne method, adding 2 cc. hydrochloric acid every four minutes and heating thirty minutes in all; (4) the Herles method, using 10.6 cc. lead nitrate solution and one-half equivalent sodium hydroxide; (5) the proposed modification to the strict Clerget method, *i. e.*, addition of 1 gram powdered zinc. Each 100 cc. of original solution contained 11.4612 grams pure cane-sugar and 0.814 gram raffinose. It was the intention to secure the same polarization as obtains in ordinary "rest" molasses with a content of 2.5 per cent. raffinose. With the exception of the Lindet-Courtonne method, 50 cc. of the original solution were taken for inversion. With the Lindet-Courtonne method, the prescribed 20 cc. were used in a 50 cc. flask and the zinc volume allowed for.

Original invert reading.	Results of normal.	Direct polarization.	Raffinose. (Lindet.)	Raffinose. (Herzfeld.)	Saccharose. (Lindet.)	Saccharose. (Herzfeld.)	
(1) —5.87	—11.74	48.60	...	2.65	....	43.70	Strict Clerget.
(2) —6.39	—12.78	48.60	...	2.00	....	44.91	Strict Clerget with char.
(3) —4.52	—11.19	48.60	2.86	3.01	43.32	43.02	Lindet-Courtonne.
(4) —5.97	—11.94	47.47	...	2.30	....	43.22	Herles.
(5) —5.86	—11.72	48.60	...	2.67	....	43.65	Proposed method.

With the strict Clerget method and use of char the increased levo-rotation is very considerable and causes a very notable variation in sucrose and raffinose from the truth. The Lindet-Courtonne method, while not showing such great variation, is still unsatisfactory and does not inspire confidence; furthermore, the writer finds inversion under its conditions more time-consuming than under any other. The modification to Clerget's method that I propose seems to give results concurring with the strict Clerget method, both here and with molasses; also in a later experiment, where the proportion of raffinose is increased.

The method next inquired into is that of Herles,[1] with the object of ascertaining its action where raffinose is present. No comparison was made of it upon inverted pure cane-sugar solutions.

Herles' chief objection to determinations by inversion as carried out up to that time was, that clarification by means of lead acetate for direct polarization and not for invert, would give wrong results, because optically active substances are precipitated in the operation for direct polarization, which remain in the inverted solution and either retain their whole optical activity or the acid changes it, or perhaps the optical activity is for the first time developed during inversion.

Degener has shown that invert sugar by evaporation, even *in vacuo*, loses its theoretical levo-rotation and finally becomes dextro-rotatory, which, by treatment with hydrochloric acid, according to Clerget, soon takes on its original levo-rotation; hence, it affects only the invert reading.

Herles states that lead nitrate remaining in excess as such has only insignificant action, and Herzfeld admits that the action is

[1] Herles, 1890: "Ueber die Bestimmung des Zuckers durch die Inversionsmethode," *Zlschr. d. Ver. für d. Rübenzuckerind. d. deutsch. Reiches*, p. 217.

small. Herzfeld states that sodium nitrate heightens the polarization and, while admitting that basic lead nitrate is a remarkable decolorizer, affirms that it carries down sugar with it, especially if the alkali be added all at once, and even a little if it be added drop-wise. Neutral salts, with the exception of the acetates, increase the levo-rotation, but the acetates reduce the free hydrochloric acid and thus lower inverting or hydrolyzing power; hence, Herles was led to consider $PbOHNO_3$ as the most suitable form. He used "a lead nitrate solution of 1.3856 specific gravity (or about saturated), and in which 1 cc. = 0.3102 lead." This could not be correct, since a stronger solution of lead nitrate, *i. e.*, specific gravity 1.414, and containing 35 per cent. lead nitrate only contains the equivalent of 0.3094 gram lead.

He distinctly states that the solution should not be alkaline, as lead saccharate would be precipitated and, while proving that resulting potassium nitrate causes increased levo-rotation, belittles it by adding that the solutions are always weak in sugar where much potassium nitrate is formed.

The solution of lead nitrate used for this experiment had a specific gravity of 1.33233 and contained the equivalent of 0.2488 gram lead or 0.398 gram lead nitrate, equaling 29.872 per cent. Accordingly, 1 cc. of this lead nitrate, to form the stipulated basic salt, will require 1.202 cc. normal sodium hydroxide, or where the standard alkali has a corrective factor of 1.061 as in this instance, 1.133 cc. A normal of molasses was weighed out, and after dilution to about 70 cc. the specified quantities of lead nitrate solution added and then the alkali solution gradually and with rotation of flask, when all was carefully diluted to exactly 100 cc. at 17.5° C. 10.6 cc. lead solution and 12 cc. alkali solution cleared the solution perfectly and left no excess of alkali.

	$Pb(NO_3)_2$ solution. cc.	NaOH solution. cc.	Direct reading.	Invert reading.	Raffinose	Saccharose.
(1)	9.00	12	50.75	—5 86	3.77	43.77
(2)	10.60	12	51.10	—5.86	3.85	43.98
(3)	12.00	12	50.99	—5.86	3.82	43.92

In samples (2) and (3), considerable lead chloride was thrown down. In such work of Herles as has come under our notice, the absence of very specific directions as to the limits of lead to be used, has left us without much information, and an intimate study

of the best conditions is not warranted, as the process has the serious defects already referred to.

The direct polarization on the same sample varies quite a little from that where lead basic acetate is used (*i. e.*, 50.6 per cent. pol.) which may be accounted for by the action of the lead salt upon the invert sugar present, which is a trifle less than 2 per cent. In the former table, where the five methods are compared, we have shown a reduction from 48.6 to 47.47 per cent. polarization where basic lead nitrate was used; hence, this is probably more than compensated for by the modified levulose rotation. To recapitulate, the results obtained so far by the different methods upon molasses, we have:

	Raffinose.	Saccharose.	
Strict Clerget, with char	3.58	43.97	
Proposed method, adding zinc	3.58	43.97	
Lindet-Courtonne, varying conditions	3.91	43.36	
with Herzfeld's formula	3.70	43.74	
Herles' method, applied	3.85	43.98	½ equivalent sodium hydroxide.

The next experiment shows (1) the absorbent effect of char upon the products of the hydrolysis of pure saccharose and pure raffinose when they are mixed in varying proportions; also (2) results by the proposed new zinc modification to the strict Clerget method, when compared with the strict Clerget method without the use of char.

Direct reading.	Invert reading without char.	Invert reading with char.	
25.62	—6.62	—7.01	Used 0.3285 gram raffinose and 6. 1835 grams sugar.
48.60	—5.87	—6.39	
48.60	—5.87	....	Proposed zinc modification. 17.1917 grams sugar and 1.221 grams raffinose.
53.40	—4.58	—5.57	
53.40	—4.57	....	Proposed zinc modification. 17.1917 grams sugar and 2.442 grams raffinose.

The zinc in the presence of the hot hydrochloric acid at 69° C. has, therefore, absolutely no effect upon the products of the hydrolysis of saccharose and raffinose. It has been found advisable to filter out, by means of a very small tuft of cotton, the residue from the 1 gram of zinc left after cooling to 20° C., with quantitative washing, of course, since the continued, slow evolution of hydrogen may disturb proper dilution to the mark.

The author wishes to add some tests made upon the correctness of Herzfeld's formula for the temperature correction for raffinose:

AS APPLIED TO HYDROLYZED HALF-NORMAL CANE-SUGAR IN 100 CC. DILUTION.

Temperature. °C.	Original reading.	Calculated to 20° C. normal inversion.
17.2	—17.06	—32.59
20.0	—16.32	—32.64
20.9	—16.07	—32.59
21.6	—15.93	—32.66

AS APPLIED TO MIXTURE OF 12.367 GRAMS CANE-SUGAR AND 0.657 GRAM RAFFINOSE IN 100 CC. DILUTION.

Temperature. °C.	Original reading.	Calculated to 20° C. normal inversion.
16.4	—14.40	—27.00
20.0	—13.50	—27.00
23.0	—12.78	—26.97

It is not advisable to make the polarization at any temperature without the use of the jacketed tube.

CARO, MICHIGAN,
April 22, 1903.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF INSECTICIDES AND AGRICULTURAL WATERS, U. S. DEPT. OF AGRICULTURE, No. 52.—SENT BY H. W. WILEY.]

A COMPARATIVE STUDY OF METHODS OF DETERMINING FORMALDEHYDE.

BY BERNARD H. SMITH.

Received June 26, 1903.

THE uses of formaldehyde have widely increased during the past few years. As a disinfectant it has come to be used in enormous quantities by health inspectors, its vapor or a dilute solution destroying many kinds of pathogenic bacteria; as a preservative it is one of the most effective and one of the most convenient to use; it is an important fungicide, the agriculturist finding it a valuable aid in combatting certain plant diseases, while as an insecticide it rids man of those insects, often more plentiful than appreciated, that choose to live in the crevices close to his food or his bed.

With the increasing use of formaldehyde, many new methods have been suggested for its quantitative determination. While some of these are rather difficult of manipulation or have other

drawbacks, others are of great value. With the view of determining, if possible, which of the commonly used methods was the most accurate and which could be applied to strong and which to weak solutions with the greatest convenience, this study was undertaken.

The solutions were made up in large quantities and kept closely stoppered, the same solutions being employed in all the methods tested. The strongest of these was the commercial formalin advertised to contain 40 per cent. formaldehyde. The others contained approximately 15 per cent., 10 per cent., 5 per cent., 1 per cent., $^1/_{10}$ per cent., and $^1/_{100}$ per cent. It should be stated that the last three were made up quite accurately, while the others contained somewhat less than the percentages given. The methods worked with up to the present time are as follows: The Blank and Finkenbeiner, the Legler, the gravimetric hexamethylenetetramine, the iodiometric, the potassium cyanide and the volumetric aniline method. In the following tables, Roman numerals are used to indicate the solutions, the strongest being I, the second strongest II, and so on to VII.

THE BLANK AND FINKENBEINER METHOD.[1]

This method is as follows:

About 3 grams of the formaldehyde solution are weighed into a flask containing 25 cc. of double normal sodium hydroxide. Then 50 cc. of hydrogen peroxide of approximately 3 per cent. strength is added cautiously, the addition lasting three minutes. The hydrogen peroxide oxidizes the formaldehyde to formic acid, which in turn is neutralized by the sodium hydroxide present, as shown in the following equation:

$$H_2O_2 + CH_2O + NaOH = NaOOCH + 2H_2O.$$

The excess of alkali is titrated with twice normal sulphuric acid, using litmus as indicator.

The following results were obtained:

I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
37.28	14.43	9.74	4.86	1.02	...	...
37.27	14.45	9.80	4.81	1.01	...	...
37.33	14.48	9.67	4.75	1.05	...	...

It is important that a few minutes should elapse after the addition of the hydrogen peroxide for the titration.

[1] *Ber. d. chem. Ges.*, **31**, 17, 2979 (1898).

THE LEGLER METHOD.[1]

A definite quantity of the formaldehyde solution is placed in a flask containing more normal ammonia than is required for the formation of the corresponding hexamethylenetetramine, which is formed as follows:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

After standing, the excess of ammonia is titrated back, using rosolic acid as indicator.

Results were obtained with this method as follows:

I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
36.99	14.44	9.62	4.55	...	...	...
37.08	14.50	9.72	4.42	...	...	...
37.14	14.40	9.82	4.33	...	...	...

Concordant results were hard to obtain with solutions of less than 5 per cent. in strength, though with the stronger solutions the results were very good. Care must be exercised to prevent loss of ammonia and the end-point is rather unsatisfactory. In this work, the determinations were allowed to stand twenty-four hours, which gives practically identical results with the one-hour boiling modification used by Craig.[2] The boiling and cooling scheme suggested by the latter largely offsets the strongest advantage of the method, that of ease of manipulation. In the comparison of this method with that of Blank and Finkenbeiner's in the same article, the Legler method is shown to give slightly higher results. Though the two methods are in "practical accord" as he suggests, in the writer's comparisons the hydrogen peroxide method almost invariably gave higher results.

THE GRAVIMETRIC HEXAMETHYLENETETRAMINE METHOD.[3]

"Ten grams of the formaldehyde solution are weighed into a flask and treated with an excess of standard ammonium hydroxide solution. The corked flask is shaken at intervals for several days. By this means the whole of the formaldehyde is converted into hexamethylenetetramine. The solution is then transferred to a weighed platinum dish, evaporated at a low heat—below 100° C., nearly to dryness, and the drying finished in a desiccator."

[1] *Ber. d. chem. Ges.*, **16**. 1333 (1883).
[2] This Journal, **23**, 638 (1901).
[3] Annual Report, Conn. Expt. Station, 1899, p. 143.

Haywood[1] has recently shown that this method is unsatisfactory, owing to the fact that there is a continual loss of weight of the hexamethylenetetramine when left in the desiccator. The following determination, made on Solution I, is typical of the results obtained by the author. After evaporating nearly to dryness, the dish was placed in a desiccator and weighed at intervals of forty-eight hours, the weights obtained giving the following percentages of formaldehyde:

Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
41.83	40.34	39.46	38.70	38.02	37.40	36.87
36.35	35.91	35.60	35.24	34.90	....	....

The weighing was here discontinued, as the last figures are obviously below the percentage of formaldehyde contained in the solution.

IODIOMETRIC METHOD.[2]

The method used is a slight modification of the one originally proposed by Romijn,[3] and is as follows:

"Thirty cc. normal sodium hydroxide and 5 cc. of the dilute formaldehyde solution are placed in a well-stoppered bottle and N/5 iodine (40 to 70 cc.) added until the liquid becomes yellow. After shaking for a minute, the liquid is acidified with 40 cc. of normal acid and the residual iodine titrated with N/10 thiosulphate. A blank titration should be made."

In the presence of an alkali, iodine acts indirectly as an oxidizing agent, giving, when formaldehyde is present, the iodide of the base and formic acid. The following equation illustrates the reaction:

$$CH_2O + 2I + 2NaOH = 2NaI + CHOOH + H_2O.$$

A solution containing as much as 5 per cent. formaldehyde may be determined without dilution by this method, provided that not more than 2 grams of the solution are used. In the following table, weighed portions of the three strongest solutions were diluted to contain approximately 1 per cent. of formaldehyde and the diluted solutions were used for the analysis.

[1] Bulletin No. 73, Bureau of Chemistry, Department of Agriculture, "Report of Referee on Insecticides and Fungicides before Official Association of Agricultural Chemists," 1902.

[2] *Zischr. anal. Chem.*, **39**, 60–63 (1900).

[3] *Ibid.*, **36**, 18–24 (1897).

I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
36.94	14.36	9.60	4.53	0.98	0.095	...
37.06	14.46	9.58	4.60	0.96	0.089	...
...	...	9.64	4.62	...	0.094	...

THE POTASSIUM CYANIDE METHOD.[1]

This is another method which is applicable to solutions containing but small quantities of formaldehyde. According to the originator of the method it depends upon the fact that formaldehyde combines with potassium cyanide to form an additional product, represented by the following:

$$CH_2O + KCN = N{\equiv}C-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-O-K.$$

In the determination, the formaldehyde is mixed with a known quantity of potassium cyanide, the latter being in excess. If this mixture is added to an excess of silver nitrate the uncombined cyanide is precipitated as silver cyanide. By using a standard silver nitrate solution and titrating the excess, we can easily calculate the amount of potassium cyanide used by the formaldehyde, and accordingly can determine the amount of formaldehyde present. The method is as follows: Ten cc. of N/10 silver nitrate are treated with six drops of 50 per cent. nitric acid in a 50 cc. flask. Ten cc. of a solution of potassium cyanide (containing 3.1 grams of KCN in 500 cc. of water) are then added and well shaken. An aliquot portion of the filtrate, say 25 cc., is titrated according to the method of Volhard with an N/10 solution of ammonium sulphocyanate for excess of silver. Another 10 cc. portion of N/10 silver nitrate is acidified with nitric acid and treated with 10 cc. of the potassium cyanide solution to which has been added a measured quantity of the dilute formaldehyde solution. The whole is made to 50 cc. and a 25 cc. filtrate from it titrated with N/10 ammonium sulphocyanate for the excess of silver, as before. The difference between these two results multiplied by 2 gives the amount of potassium cyanide that has been used by the formaldehyde in terms of N/10 ammonium sulphocyanate.

[1] *Ztschr. anal Chem.*, **36**, 18–24 (1897).

In obtaining the following results, all solutions containing more than 1 per cent. were diluted.

I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
37.12	14.40	9.61	4.60	1.002	0.102	0.0099
37.07	14.55	9.63	4.54	0.972	0.102	0.0099
37.18	14.48	9.59	4.64	0.99	...	...

With solutions of 1 per cent. strength it was found necessary to use 15 cc. of silver nitrate. It is preferable to add six or eight drops of nitric acid instead of two as used by Romijn, as the titration is sharper when the solution is more strongly acid. In working with Solution VII, a 200 cc. flask was used instead of the 50 cc. flask, and 100 cc. of the filtrate titrated.

Attention should be called to the fact that the directions for using this method, as given in Allen's "Commercial Organic Analysis,"[1] which were taken from a review that appeared in the *Analyst*,[2] are not explicit. The essential feature of the method being that formaldehyde forms an additional product with potassium cyanide, the formaldehyde solution must be mixed with the cyanide solution and the mixture added to the silver nitrate. This is not made clear in the article referred to. In the same translation another error is introduced in that the operator is told to dilute to 500 cc. instead of 50 cc., as in the original article.

THE ANILINE VOLUMETRIC METHOD.[3]

If formaldehyde be treated with an aqueous solution of aniline, methylene aniline is precipitated, as illustrated by the following:

$$C_6H_5NH_2 + CH_2O = C_6H_5NCH_2 + H_2O.$$

Following is the method of procedure:

"Four hundred cc. of aniline solution, containing 3 grams of aniline per liter, are placed in a flask and 1 cc. of formaldehyde solution added, by drops, with shaking. The mixture is made up to 500 cc. and after some time filtered. The excess of aniline is then estimated in 50 cc., taking as the end-point that at which the red color acquires a strong bluish tone, remaining unaltered on further addition of acid."

The end-point in this titration is quite indefinite, the "bluish

[1] Third edition, p. 221.
[2] *Analyst*, **22**, 221 (1897).
[3] *Pharm. Ztg.*, **40**, 611 (1895).

tone" developing very gradually. After repeated unsuccessful trials, the attempt to use the method was abandoned.

Four of the methods are summarized in the following table, which gives the average percentages of formaldehyde found in the solutions used, and also shows the working range of each when no dilutions are made.

Method.	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.	VII. Per cent.
H_2O_2	37.33	14.45	9.74	4.81	. .	...	...
Legler	37.07	14.45	9.65	4.43	...	...	...
Iodiometric	...	...	...	4.55	0.97	0.093	...
Potassium cyanide	...	...	...	...	0.988	0.102	0.0099

The following conclusions may be drawn from the comparisons made:

First, the Blank and Finkenbeiner method is very satisfactory for strong solutions.

Second, the Legler method, while not giving quite as high results as the former, is fairly satisfactory.

Third, the gravimetric hexamethylenetetramine method is practically worthless.

Fourth, the iodiometric and the potassium cyanide methods give good results on dilute solutions. It should be remembered that in diluting strong solutions to the range of these methods, a small error in weighing may be considerably multiplied. The potassium cyanide method is best adapted to the estimation of very small quantities of formaldehyde, it being possible to determine with accuracy 1 part in 100,000.

Fifth, in the hands of the writer, the end-point of the aniline volumetric method was impossible to read.

Since preparing the foregoing paper there has come to my attention an article reviewed in the *Zeitschrift für angewandte Chemie*, April 7, 1903, the original article having appeared in the *Deutsche Gerber Zeitung*, 1-4, 6, 8, 12. The author, C. Wallnitz, has compared seven commonly used methods of determining formaldehyde and has arrived at the following conclusions: That the hydrogen peroxide and the iodine methods are superior to the others tested when the reagents are freshly prepared; that the ammonium chloride[1] method, the Legler ammonium method,

[1] Hugo Schiff: *Chem. Ztg.*, **27**, 14, Jan. 7, 1903.

and the aniline volumetric method all lack distinctness in the end-point readings; and further, that the gravimetric silver nitrate method of L. Vanino is practically useless, not being exact in its results.

The potassium cyanide method, which is one of the most accurate, was not included in this investigation.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, LABORATORY OF INSECTICIDES AND AGRICULTURAL WATERS, NO. 53.—SENT BY H. W. WILEY.]

THE ESTIMATION OF FORMALDEHYDE IN MILK.

BY BERNARD H. SMITH.

Received June 26, 1903.

FORMALDEHYDE is added to milk as a preservative more than to any other food. Its quantitative determination in this universally used product is, therefore, of the greatest importance.

Formaldehyde distils slowly even from an aqueous solution. When it is added to milk, and has combined to a greater or less extent with the albuminoids present, the rate of distillation is naturally slower still. Should the distillation be continued until four-fifths of the volume taken has been driven over, which is as much as can be distilled conveniently, all of the formaldehyde will not have been recovered. The distillation is, moreover, a troublesome one, owing to the frothing and bumping of the boiling milk. The writer has found that the latter can be largely obviated by using with the ordinary condenser a 500 cc. Kjeldahl nitrogen flask and a round, flat evaporating burner. With this apparatus the distillation proceeds quietly and without difficulty.

In an article by Leonard and Smith[1] results are given showing that the addition of "a few drops of dilute sulphuric acid" largely increased the amount of formaldehyde recovered during the first part of the distillation. In their experiments 100 cc. of milk were used containing 1 part in 100,000 of formaldehyde, and three portions of the distillate of 20 cc. each were collected. Nearly one-third of the formaldehyde present was found in the first 20 cc. of the distillate.

In attempting to make use of this suggestion the writer found that the amount of sulphuric acid present had a great influence on the amount of formaldehyde found in the first 20 cc. of the distillate, as is shown by the following table:

0.3 cc. dilute H_2SO_4 (1 : 3). Per cent.	1 cc. dilute H_2SO_4 (1 : 3). Per cent.	5 cc. dilute H_2SO_4 (1 : 3). Per cent.	20 cc. H_2SO_4 not diluted. Per cent.
24	32.5	18	None

This would tend to show that in obtaining maximum results the quantity of sulphuric acid added is an important factor, and that while the milk should be more than simply acid, an excess of

[1] *Analyst*, **22**, 5 (1897).

acid is to be avoided. In subsequent work, 1 cc. of sulphuric acid of a dilution of 1 : 3 was used with 100 cc. of milk. One-fifth portions, or 20.02 cc. were collected and analyzed, using the potassium cyanide method.[1]

The following work was undertaken in an attempt to decide as to whether milk, containing formaldehyde, would yield the same amounts in the first 20 cc. of distillate, after standing some time, as upon immediate distillation, and also as to whether different samples of milk containing various amounts of formaldehyde would give it up in the first 20 cc. of the distillate in direct proportion to the amount they originally contained.

Four samples of fresh milk were treated with formaldehyde so that they contained 1 part in 5,000, 1 part in 10,000, 1 part in 25,000, and 1 part in 50,000. One hundred cc. portions of each were distilled immediately, others at the end of twenty-four and forty-eight hours. The latter in the intervening time were kept in a cool place. The following percentages of the total formaldehyde added were obtained in the first 20 cc. of the distillates.

	1 part in 5,000. Per cent.	1 part in 10,000. Per cent.	1 part in 25,000. Per cent.	1 part in 50,000. Per cent.	Averages. Per cent.
Determined immediately..	31.50	33.90	36.10	41.00	35.62
After 24 hours	30.60	32.00	32.80	37.50	33.22
After 48 hours	30.75	31.50	35.00	36.00	33.31

From the average column on the right, it is seen that the average results on milk that has stood a short time after the addition of the formaldehyde are very close to $33^1/_3$ per cent. The next column shows that the samples of milk containing the least formaldehyde give the highest percentages of the total amount present. The table shows, furthermore, that if milk containing formaldehyde is kept cool, it may stand one or two days at least without altering the amount obtained on analysis. A trial proved that when milk containing formaldehyde is subjected to a warm and varying temperature, the amount of formaldehyde recovered by distillation in the first 20 cc. decreases so that at the end of forty-eight hours only 18 or 20 per cent. will be found, instead of approximately 33.

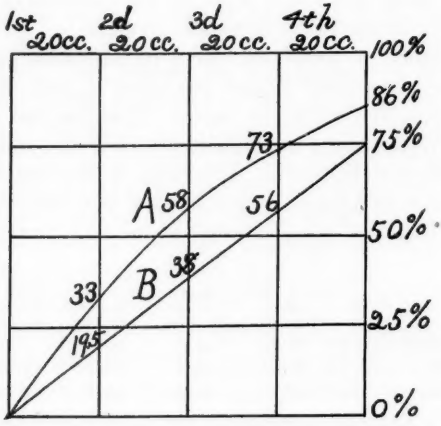
The following chart, the data for which were compiled from a number of analyses, gives the curves showing the rapidity of the

[1] See the preceding paper, p. 1032.

distillation of formaldehyde from milk containing 1 part in 10,000. The ordinates represent the per cent. of the total formaldehyde present, and the abcissas the amount of distillates.

The line A is the curve obtained from milk after the addition of 1 cc. of the dilute acid, while B is the one obtained from milk without the addition of acid.

In summarizing, it may be said that considerable time and trouble may be saved by using a Kjeldahl flask and a round, flat



evaporating burner in the distillation of milk; that the quantity of sulphuric acid added has a decided effect upon the amount of formaldehyde obtained in the first part of the distillation; that if the treated milk is kept in a cool place, the percentage of formaldehyde found will remain practically constant for at least forty-eight hours; and that where 100 cc. of milk are treated with 1 cc. of sulphuric acid of a dilution of 1 : 3 and distilled, the first 20 cc. of the distillate will contain very close to $33^1/_3$ per cent. of the total formaldehyde present.

The author wishes to acknowledge the valuable suggestions of Dr. H. W. Wiley, under whose direction this and the foregoing article have been prepared.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 73.]

THE ELECTROLYTIC PRECIPITATION OF NICKEL FROM PHOSPHATE SOLUTIONS.[1]

BY WALTER T. TAGGART.

Received July 6, 1903.

NICKEL has been quantitatively precipitated in the electrolytic way from various electrolytes.[2] The purpose of this particular investigation was to ascertain the exact conditions under which this metal could be deposited from phosphate solutions without carrying down phosphorus with it; also to effect, if possible, separations of nickel from other metals in the same electrolyte. The method pursued consisted in precipitating nickel sulphate solutions with varying amounts of disodium hydrogen phosphate of 1.038 specific gravity, dissolving the precipitate in phosphoric acid of 1.347 specific gravity, and after dilution with water, electrolyzing the solutions with varying current and pressure conditions.

The precipitations were made in platinum dishes—the cathodes, while flat platinum spirals were used as anodes. The deposits were treated as ordinarily directed in electrolytic work. The details of more than forty experiments appear in those recorded in the accompanying tables, with sufficient minuteness to enable any person, so desiring, to repeat them with the confidence of obtaining like satisfactory results.

EXPERIMENTS.

	1.	2.	3.	4.	5.	6.
$N.D_{100}$	2.0	2.0	4.0	4.0	2.0	3.0
Volts	6	6	6	6	6	6
Dilution, cc.	225	125	200	250	125	175
Temperature	50°	65°	65°	55°	65°	65°
Time, hours	7	7½	8¼	9½	6¾	8½
Na_2HPO_4, cc.	90	90	130	180	90	135
H_3PO_4, cc	4.5	4.5	9.0	9.0	4.5	6.75
Nickel taken, gram	0.2166	0.2166	0.4332	0.4332	0.2166	0.3249
Nickel found, gram	0.2163	0.2161	0.4298	0.4321	0.2165	0.3253

[1] From the author's thesis for the Ph.D. degree.

[2] See Smith's "Electrochemical Analysis," p. 91, third edition, 1902.

	7.	8.	9.	10.	11.
$N.D_{100}$	4.0	2.0	3.0	3.0	4.0
Volts	6	6	6	6	6
Dilution, cc	250	125	175	175	250
Temperature	55°	65°	70°	62°	55°
Time, hours	9½	7¼	9	9½	9¾
Na_2HPO_4, cc	180	90	135	135	180
H_3PO_4, cc	9.0	4.5	6.75	6.75	9.0
Nickel taken, gram	0.4332	0.2166	0.3249	0.3249	0.4332
Nickel found, gram	0.4327	0.2163	0.3247	0.3251	0.4321

	12.	13.	14.	15.	16.
$N.D_{100}$	1.–1.75	1.4.–1.8	1.0–1.5	1.4–1.8	1.25
Volts	6	6	6	6	6
Dilution, cc	125	125	175	175	175
Na_2HPO_4, cc	90	90	90	135	90
H_3PO_4, cc	4.5	4.5	4.5	6.75	4.5
Nickel taken, gram	0.2176	0.2176	0.2176	0.3264	0.2176
Nickel found, gram	0.2179	0.2181	0.2176	0.3271	0.2180
Temperature	56°	50°	50°	50°	50°
Time, hours	7	7	7	9¼	7¼

	17.	18.	19.	20.	21.
$N.D_{100}$	1.4–1.8	1.25–1.6	1.25–1.6	0.25–1.6	1.25–1.6
Volts	6	6	6	6	6
Dilution, cc	225	230	230	230	230
Na_2HPO_4, cc	135	180	180	180	180
H_3PO_4, cc	6.75	9.0	9.0	9.0	9.0
Nickel taken, gram	0.3264	0.4352	0.4352	0.4352	0.4352
Nickel found, gram	0.3271	0.4353	0.4355	0.4353	0.4354
Temperature	50°	50°	50°	50°	50°
Time, hours	9	10	10	10	10

In every case except No. 1 and No. 11 the precipitation was complete. The success of the process depends greatly on keeping the dish covered and washing down its sides with water at frequent intervals, to supply the loss by evaporation and to prevent the phosphate of nickel from separating out on the dish.

These results need no further explanation. The deposits were equal in appearance, if not superior, to any deposits of nickel ever obtained in this laboratory. Those of 0.4352 gram of nickel, when dissolved in nitric acid and tested with ammonium molybdate, showed but a trace of phosphorus, which is without influence, for solutions electrolyzed by Fresenius and Bergmann's method[1] gave exactly the same amount of nickel.

The influence of elevation of temperature is shown in the following examples:

[1] *Ztschr. anal. Chem.*, **19**, 320.

	22.	23.	24.
$N.D_{100}$	2.4–2.8	2.25	1.80–2.75
Volts	6	6	6
Dilution, cc	125	175	225
Temperature	88°	88°	88°
Time, hours	2½	5	6¼
Na_2HPO_4, cc	90	135	180
H_3PO_4, cc	4.5	6.75	9
Nickel taken, gram	0.2176	0.3264	0.4352
Nickel found, gram	0.2167	0.3265	0.4331

	25.	26.	27.
$N.D_{100}$	1.80–2.75	1.80–2.75	1.80–2.75
Volts	6	6	6
Dilution	125	125	175
Temperature	82°	80°	80°
Time, hours	3½	4	5½
Na_2HPO_4, cc	90	90	135
H_3PO_4, cc	6.75	5.6	9.1
Nickel taken, gram	0.2176	0.2176	0.3264
Nickel found, gram	0.2150	0.2161	0.3255

The precipitation was only complete in 23. If the conditions there given be adopted, satisfactory results can be obtained in a considerably shorter time than is required when working at the ordinary temperature.

The separation of nickel from manganese, iron, aluminum and chromium was considered. The results were negative in each instance.

Hence, it may be concluded from what has preceded that nickel free from phosphorus can be completely precipitated from a solution of nickel sulphate containing disodium hydrogen phosphate and free phosphoric acid, a mineral acid; that the deposit is equal to that precipitated by any other known method; that the time factor can be reduced by raising the temperature and that nickel can not be separated from manganese, iron, aluminum or chromium in phosphoric acid solutions. It was found that chromium salts in the presence of disodium hydrogen phosphate and free phosphoric acid are oxidized to chromates by the electric current.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 74.]

THE REDUCTION OF NITRIC ACID IN METALLIC NITRATES TO AMMONIA BY THE ELECTRIC CURRENT.[1]

BY WM. H. EASTON.

Received July 6, 1903.

LUCKOW announced[2] that "dilute nitric acid between two platinum poles will not be reduced to ammonia either alone or in the presence of dilute sulphuric acid. But, if copper sulphate in solution be added to the dilute nitric acid, then the formation of ammonium sulphate occurs, when the liquid is electrolyzed." Vortmann[3] endeavored to make this a quantitative method for the estimation of nitric acid.[4]

This is his description of the analysis of a nitrate:

"The solution of the nitrate is placed in a platinum vessel with a sufficient amount of pure copper sulphate and it is then electrolyzed. It is advantageous to use a feeble current (1 to 2 cc. of oxyhydrogen gas per minute). When all of the copper is deposited, the residual liquid is evaporated to a small bulk and the ammonia distilled off as usual."

Simple as these directions are, many persons have failed to get satisfactory results. Numerous inquiries have been made at this laboratory for fuller details; hence, the writer was directed to give the problem attention, more particularly with reference to the factors which have never before been studied in this particular example, *viz., amperage, time, current density at the anode, the amount of copper sulphate essential, the amount of nitrate* and *the character of the cathode.*

Potassium nitrate was the first nitrate analyzed. The conditions were:

Potassium nitrate	0.5 gram
Copper sulphate	0.5 gram
Cathode	Platinum or copper plate of 100 square centimeters area.
Amperes	0.15 to 3.0
Time	for 3.0 amperes, 1¼ hours for 0.15 ampere, 8½ hours

[1] From the author's thesis for the Ph.D. degree.

[2] *Zischr. anal. Chem.*, **19**, 11 (1880).

[3] *Ber. d. chem. Ges.*, 1890, p. 2798.

[4] See Smith's "Electrochemical Analysis." p. 194, third edition, 1902.

Volts: From 3 to 8, depending upon the current strength.
Dilution: 150 cc.
Sulphuric acid (sp. gr. 1.062): 30 cc.

The following percentages of nitrogen reduced to ammonia were obtained, the theoretical per cent. in potassium nitrate being 13.86:

13.70	13.60	13.50	13.65
13.74	13.68	13.77	13.54
13.62	13.43	13.32	13.68
13.43	13.78	13.50	

It was further learned, from additional experiments, that the time factor could be reduced to two and one-half hours by employing a current of 1 ampere. Further, in no trial did the variation of the current density at the anode have any influence on the amount of nitrogen reduced to ammonia. The amount of copper sulphate needed can easily be deduced from the results which follow, the other conditions being as recorded above.

Grams KNO_3.	Grams $CuSO_4.5H_2O$.	Per cent. N reduced.
0.5195	0.1098	11.44
0.5243	0.2083	12.23
0.5041	0.2600	13.33
0.4950	0.3600	13.13
0.5676	0.5691	13.74

Theory, 13.86 per cent.

The quantity of potassium nitrate was also varied, equal weights of copper sulphate being taken, while the other conditions continued as before:

Grams of potassium nitrate.	Grams of nitrogen reduced.	Per cent. of nitrogen reduced.
0.1053	0.0148	14.01
0.1063	0.0148	13.93
0.2592	0.0348	13.43
0.2616	0.0356	13.62
0.5027	0.0693	13.77
0.5723	0.0789	13.78

The method seems accurate enough for all quantities. The actual weights of nitrogen show the delicacy of the method.

In the preceding experiments platinum dishes were the cathodes. The copper deposits were compact and readily washed. When copper plates of 100 sq. cm. area were substituted for the dishes and suspended in the nitrate solution, contained in beakers, the

precipitated copper was spongy, did not adhere well, and some difficulty was had in washing it. The percentages of reduced nitrogen ranged from 13.04 to 13.44 (theory, 13.86). Lead plates of 100 sq. cm. area were also tried. The copper was precipitated upon them in a very unsatisfactory form. They were also attacked, and the nitrate was never completely reduced when they were employed. No better success was met with mercury cathodes, while nickel (36 sq. cm. area) proved very satisfactory.

The time necessary for the reduction of 0.5 gram of potassium nitrate was two and one-half hours, when using a current of 1 ampere. Would 3 or 5 amperes produce the desired result in a shorter period? Accordingly, a solution of 0.5009 gram of potassium nitrate, 1 gram of copper sulphate and 40 cc. of sulphuric acid (sp. gr. 1.062) was electrolyzed for thirty minutes with a current of 3 amperes. The copper was not completely precipitated and only 6.68 per cent. of the nitrogen was reduced to ammonia. Upon increasing the current to 5 amperes and allowing it to act for thirty minutes the percentage of reduced nitrogen was 13.22, although not quite all of the copper was precipitated.

It was a matter of considerable interest to learn the behavior of other nitrates than those of the alkali metals. Copper nitrate electrolyzed alone—without copper sulphate—yielded 11.52 and 11.35 per cent. of nitrogen (theory, 11.59 per cent.) to the current. In the case of silver nitrate, complete reduction was not reached until after the addition of an equal amount of copper sulphate. This proved to be the case with cobalt and cadmium nitrates.

Observing the conditions given on p. 1042, employing at the same time a current of $N.D_{100} = 1$ ampere, the reduction will proceed rapidly and the method will prove very helpful in many instances.

Experiments have been made with a rotating anode which suggest the possibility of reducing quite considerably the time factor in this method.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 75.]

THE ELECTROLYTIC DETERMINATION OF MANGANESE AND ITS SEPARATION FROM IRON AND ZINC.[1]

BY GEORGE P. SCHOLL.

Received July 6, 1903.

THE deposition of manganese as peroxide for quantitative estimations by electrolysis has been the subject of a great deal of investigation, as reference to its voluminous literature will disclose.[1]

It was believed that formic acid, because of its simple constitution, would prove an excellent electrolyte and that under the right conditions very satisfactory results would be obtained with it. It was, therefore, tried with the addition of sodium formate.

The electrolysis was conducted as follows: Ten cc. of a solution of manganese sulphate (= 0.1100 gram of metal) were mixed with 5 cc. of formic acid (sp. gr. 1.06), 10 cc. of a sodium formate solution, containing 1 gram of the salt, and diluted to 130 cc. with water so that the liquid covered 100 sq. cm. of the surface of the dish. The dish was made the anode and a flat spiral the cathode, arranged as nearly as possible equidistant from the sides and the bottom of the dish to obtain as uniform a distribution of the current as possible. The current equaled 1.4 amperes, the pressure between the electrodes being 12 volts at the beginning but decreasing to 8.6 volts at the end. It acted for one and one-half hours, when, no further precipitation taking place, the liquid was siphoned off and replaced by water without interrupting the current. The deposit showed a deep black, shining color. It adhered firmly to the dish and was not detached on washing. Smith's statement[1] that it is useless to try to obtain a definite compound by drying the deposit and that ignition to the protosesquioxide is necessary to secure definite and concordant results was found to be true. The results of four determinations made in exactly the same manner were:

Electrolyte.	Time.	Temperature.	$N.D_{100}$ at anode.	Voltage.	Mn found. Gram.
10 cc. $MnSO_4$ + 5 cc. HCOOH 1.06 sp. gr. + 10 cc. = 1 gm. sodium formate.	$1^1/_2$ hrs.	Ordinary temp. at start, heated up by action of current to 40°–50° at the end.	1.4	12 volts at start to 8.6 volts at end.	0.1100 0.1105 0.1104 0.1101

[1] From author's Ph.D. thesis.

[2] Consult Smith's "Electrochemical Analysis," Third edition, 1902.

[3] "Electrochemical Analysis," Third edition, p. 96.

These demonstrated that it was quite possible to deposit the manganese completely in the presence of formic acid, even if the latter was present in amounts considerably above those given by Kaeppel as the maximum.[1]

According to Classen[2] it is necessary to weigh the platinum dish after the deposit of peroxide has been removed from it, as the dish suffers a diminution of weight during electrolysis, amounting to about 1 mg. With the electrolyte used in the preceding experiments this did not take place, the dish losing either no weight at all or at the most only 0.1 mg.

The deposits were weighed without any difficulty. They slowly attracted moisture, however, and on standing over night gained perceptibly in weight.

Experiments were also conducted with low voltage to ascertain the effect of a lower current and consequently lower current density upon the deposit. The character of the latter remained unchanged. The application of heat (50° to 55°) proved harmful. It was also ascertained that large quantities of sodium formate retarded the precipitation quite decidedly. Further, the weights of the deposits increased as the amount of sodium formate was increased. Indeed, it was scarcely possible to weigh those obtained where 2.5 grams of sodium formate had been present, even after ignition over a blast-lamp. The most reasonable explanation of this fact seemed to be that the sodium formate was partly decomposed by the current, with the formation of caustic soda at the cathode. This caustic soda, being specifically heavier than the electrolyte, fell to the bottom of the dish anode, and was enclosed and held mechanically by the precipitating manganese peroxide. It should be noted in this connection that careless washing of the deposit was entirely excluded.

The next step was, consequently, to do away with the source of error traceable to the addition of sodium formate and to try formic acid alone. The voltage required was high, on account of the low conductivity of the formic acid, it being 17.5 volts between the electrodes at the start, with a current strength of 1 ampere. As the solution became very warm in about an hour, the voltage was decreased to 7.9 volts, giving an amperage of 0.8. The deposit did not come down as quickly as when sodium formate was pres-

[1] *Ztschr. anorg. Chem.*, **16**, 268.
[2] "Ausgewählte Methoden," p. 369.

ent, but the manganese was all out after four hours. It was further found that the precipitate was absolutely non-hygroscopic after ignition, and could be weighed with perfect ease. It was left purposely exposed to the action of the atmosphere over night and reweighed on the following morning, when the weight was found to be the same. The appearance of the deposit was like that noticed before. As the determinations with employment of the spiral of platinum wire as cathode had necessitated such a high potential betweeen the electrodes in order to obtain the necessary strength of current and caused thereby objectionable heating of the electrolyte, it was decided to adopt some means to get along with as low a voltage as possible, and which would give the necessary current. Accordingly, a so-called basket electrode was used. This was a platinum dish, which conformed in shape to the interior surface of the roughened dish on which the precipitation of manganese peroxide took place. It had an area of 60 sq. cm. and was perforated with holes to allow of a better egress of the gases set free during electrolysis and a better mixing of the solution. The following table gives the results of some experiments carried out with varying quantities of formic acid and varying quantities of manganese.

The deposits obtained were all very satisfactory and adherent. A slight disposition towards loosening was noticeable with those in which there was 0.2880 gram of manganese protosesquioxide present. It was, however, very slight, and, owing to the scaly nature of the material, it was quite easy to filter it out quickly on a small filter, wash, dry and remove it from the filter and add it to the bulk of the material in the dish, together with the ash of the filter-paper.

It is also apparent from the above table that the addition of more than 5 cc. of formic acid of 1.06 specific gravity has no beneficial effect. On the contrary, larger amounts of formic acid tend to retard the precipitation. Much less than 5 cc. of formic acid cannot be used, as there is a tendency to form flakes of a brown precipitate around the cathode, which have to be brought into solution again by the addition of more formic acid.

Other experiments were made to learn whether the addition of ammonium formate would have any accelerating or otherwise beneficial effect on the deposit. Such was not found to be the case. When chrome alum was introduced into the electrolyte, the

Manganese taken. Gram.	Manganese found. Gram.	Formic acid (sp. gr. 1.09).	Time.	Temp.	N.D$_{100}$.	Voltage.	Character of deposit.
0.1034	0.1036	5	2½	ordinary, rising toward the end.	0.8 to 1.0	7.6 at end.	satisfactory, adherent
0.1034	0.1034	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1034	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1035	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1033	5	2½	"	0.8 to 1.0	7.6	"
0.1034	0.1035	10	3½	"	0.8 to 1.0	7.2	"
0.1034	0.1034	10	3½	"	0.8 to 1.0	7.2	"
0.1034	0.1032	15	5	"	0.8 to 1.0	7.0	"
0.1551	0.1551	5	3¾	"	0.8 to 1.0	7.3	"
0.1551	0.1552	5	3¾	"	0.8 to 1.0	7.3	"
0.1551	0.1550	7½	4	"	0.8 to 1.0	7.0	"
0.1551	0.1449	10	5	"	0.8 to 1.0	6.8	"
0.2068	0.2069	5	5	"	0.8 to 1.0	6.6	" a trifle loose on washing.
0.2068	0.2069	5	5	"	0.8 to 1.0	6.6	" "
0.2068	0.2070	10	6¾	"	0.8 to 1.0	5.6	" "
0.2068	0.2071	10	6¾	"	0.8 to 1.0	5.6	" "
0.2068	0.2071	15	7	"	0.8 to 1.0	5.4	" "

results were also very unsatisfactory. It may, therefore, be briefly concluded that:

(1) The statement of Kaeppel, that it is not possible to precipitate manganese completely in the presence of formic acid and that more than five drops of this acid prevent the deposition of manganese peroxide entirely, is not borne out by the experimental facts.

(2) It is possible to obtain the deposit of peroxide from a formic acid solution in a beautifully adherent and satisfactory form, which can be washed and ignited without any trouble.

(3) Formic acid is a better electrolyte than acetic acid, it being possible, according to Classen,[1] to deposit not more than 0.08 gram of manganese in the form of peroxide when the latter is used.

The influence of other organic acids upon the precipitation of manganese was also studied. These were propionic, butyric, malonic, succinic, tartaric and fumaric acids. Fumaric acid, alone, yielded results which were in the least satisfactory. The deposits were never entirely adherent.

(1) SEPARATION OF MANGANESE AND IRON.

It seemed very probable that iron might be easily separated from manganese in a formic acid solution. This hope, however, seemed doomed to disappointment, for when a separation was tried under the conditions which had proved most successful for manganese alone, not much of a result was obtained, even upon continuing the electrolysis for twelve hours. The electrolyte consisted of 10 cc. of a ferric ammonium sulphate solution, containing 0.1000 gram of metallic iron, 10 cc. manganese sulphate, containing 0.1034 gram manganese and 5 cc. formic acid. The basket electrode served as cathode and the dish as anode. A long series of experiments was made, but the results were far from quantitative. It was also tried to see whether a uniform current density at the electrodes would prove beneficial, and therefore a number of experiments were made by introducing the solution into a beaker glass and suspending in it two platinum gauze electrodes, arranged exactly opposite each other. This was unsuccessful. It was noticed in all of this work that, in order to obtain the iron free from manganese, it was absolutely essential to have the current density at the cathode entirely uniform, that is to say, all parts of the cathode had to be equidistant from the anode surface.

[1] "Quantitative Analysis by Electrolysis," p. 149.

If there was one point of the cathode nearer to the anode, there was danger of some manganese peroxide being deposited there. Perhaps this fact explains why it has not been possible to obtain concordant results with methods proposed by different investigators up to the present time.

Electrodes of sheet platinum were also tried. The results were disappointing. It was next decided to ascertain whether the separation of the two metals could be made by retarding or preventing the deposition of manganese dioxide altogether. Hence the electrolysis was conducted thus: The electrolyte contained 10 cc. of manganese sulphate (= 0.1034 gram of manganese) and 10 cc. of a ferric ammonium sulphate solution containing 0.1003 gram of iron. To this were added 10 cc. of an ammonium formate solution, and 10 cc. of an ammonium sulphate solution containing 3 grams of this salt. 1 cc. of a solution of 45 per cent. formaldehyde was also added. The platinum dish was used as cathode, and the basket electrode, which had been used before, was introduced as anode. The solution was then made up to 130 cc., and the electrolysis conducted in the cold, with a voltage between the electrodes of 3.5 and an amperage of 1.4, the $N.D_{100}$ at the anode being consequently 2.33 and at the cathode 1.4. The iron was deposited in from three to five hours in a very satisfactory form, and not a trace of it could be detected in the solution. It proved to be entirely free from manganese. A little manganese peroxide precipitated on the anode in a very adherent form, but only from 0.0055 to 0.006 gram of peroxide had deposited at the end of the electrolysis when the iron was fully precipitated. No peroxide was suspended in the electrolyte. The solution was colored red from the permanganic acid formed. The deposit of iron contained varying and sometimes considerable amounts of carbon, which proved, however, no obstacle to a successful determination of this metal, as it was easily possible to dissolve the deposit off the dish very quickly by introducing distilled water and a few cubic centimeters of concentrated sulphuric acid. The solution was then transferred to a beaker and boiled for a few minutes in order to get rid of the hydrocarbons. A little granulated zinc was added in order to reduce any iron which might have become oxidized, and the solution was then titrated with a very dilute standardized solution of potassium permanganate. The whole manipulation in this way consumed, perhaps, less time than the

Iron present. Gram.	Iron found. Gram.	Manganese present. Gram.	Tartaric acid. Gram.	Ammonium formate. cc.	Formaldehyde 45 per cent. cc.	Ammonium sulphate. Grams.	Time.	Temp.	N.D100.	Voltage.
0.1003	0.1001	0.1034	1	10	1	3	4	ordinary	1.4	3.5
0.1003	0.1003	0.1034	1	10	1	3	4½	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	3½	"	1.4	3.5
0.1003	0.0999	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.1003	0.1001	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0983	0.1034	1	10	none	3	4	"	1.4	3.5
0.0982	0.0982	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0978	0.1034	1	10	1	3	4	"	1.4	3.5
0.0982	0.0980	0.1034	1	10	1	3	4	"	1.4	3.5

drying and weighing of the dish would have done. The following results were obtained in this manner:

The solution, when removed, had a fishy smell, due to decomposition products of the formaldehyde. The addition of the latter was discontinued after it had been shown by experiment that its presence had no influence on the result. The fishy smell of the solution did not appear after its removal. Results with and without formaldehyde are given in the above table.

Though it was shown by these experiments that, in an electrolyte composed as above, a successful separation of the iron and manganese could be accomplished in much less time than by the method of Kaeppel, yet it was felt that only half of the problem had been solved in this way. The fact that the manganese could not be determined electrolytically after the iron was all out, and that it had to be held up and thus be prevented from deposition, were sufficient stimulants to renew the effort of finding a method by which the two metals could be determined simultaneously.

The experiments with formic acid were, therefore, resumed. The electrolysis was carried out in the roughened platinum dish with the basket platinum electrode, it having been found by repeated trials that a spiral cathode could not be used, as there was invariably a precipitate of manganese oxide on it, especially on the outer rim, which was nearest to the anode, due evidently to a high current density at the cathode. The electrolyte was made up in such a manner that 10 cc. of a solution, containing 0.1 gram of sodium sulphite, were introduced into the dish and the ferric ammonium sulphate, containing 0.0997 gram of iron, was added. The solution immediately acquired a very dark red color. The 10 cc. of manganese sulphate were then introduced, and after that the formic acid solution. Five cc. of the latter acid of 1.06 sp. gr. were found to answer well. It was discovered that the addition (twice) of 1 cc. of a sodium sulphite solution, containing 0.1 gram in 1 cc. for every half hour at the beginning, and an addition of an equal amount every hour until the iron was out, was very beneficial. A very good indication of the gradual deposition of the iron is furnished by the fact that on each addition of sodium sulphite the color of the solution deepens quite perceptibly, the color getting paler, the less iron there is present. It should then be watched and tested for iron from time to time,

until no further reaction is obtained. Care must be taken in this connection that the electrode with the iron deposit on it be taken out as soon as the reaction of iron ceases. If that is not done, there is danger of some of the iron going into solution again. The basket electrode is then removed, washed off, and an auxiliary spiral electrode inserted as quickly as possible into the solution in order to prevent the manganese peroxide from dissolving in the electrolyte. Care must be taken during the time that this spiral electrode is in the solution, to insert resistance into the circuit, so as to cut down the current to 0.1 ampere or less, in order to prevent any precipitation on the spiral electrode. If this precaution be not taken, there will invariably be a brown-looking deposit on the electrode. The basket electrode with the deposit of iron on it is introduced into a small beaker and covered with distilled water. A few cubic centimeters of concentrated sulphuric acid are then added, when the solution of the iron will take place rapidly. The basket is then washed off and reintroduced into the electrolyte, after the spiral electrode has been taken out. Five cc. of formic acid of 1.06 sp. gr. are added, and the current raised to its original value again for the purpose of precipitating the rest of the manganese. The results obtained are shown in the following table and are very satisfactory and concordant.

Fe present. Gram.	Fe found. Gram.	Mn present. Gram.	Formic acid 1.06. cc.	Sodium sulphite.	Time.	Temp.	N.D_{100} cathode.	Voltage.
0.1010	0.1008	0.0988	5	6 additions 0.1 g. each	$4^1/_2$	ordinary	1.2	4.4
0.1010	0.1008	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1010	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1008	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0494	5	0.1 "	$4^1/_2$	"	1.2	4.4
0.1010	0.1007	0.0494	5	0.1 "	$4^1/_2$	"	1.2	4.4
0.1010	0.1010	0.0494	5	0.1 "	5	"	1.2	4.4
0.1010	0.1009	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1007	0.0988	5	0.1 "	5	"	1.2	4.4
0.1010	0.1011	0.0988	5	0.1 "	5	"	1.2	4.4

It was thus established that the separation of iron and manganese could also be effected in an electrolyte, consisting mainly of formic acid. It was noticed, however, that while the sodium sulphite was very effective, so far as the iron was concerned, it retarded the deposition of the manganese. The compiete pre-

cipitation of 0.0988 gram of manganese required from thirteen to fourteen hours, a period almost too long to make the method of practical value. Therefore, further experiments were undertaken to reduce the time actually required for the precipitation of the manganese after the previous removal of the iron. Various means were adopted to accomplish this.

An experiment was conducted in the usual manner with addition of sodium sulphite, until the iron was out and removed. Ten cc. of an ammonium acetate solution were then added and the electrolysis continued. The result was quite surprising, for after two hours the level of the solution was raised, and it was observed that there was no further precipitation of manganese peroxide. When the solution was tested, no manganese was found to be present. The time of deposition of the peroxide had thus been reduced from thirteen or fourteen hours to seven hours. The deposit weighed 0.0992 gram while 0.0988 gram was present.

It was recognized that the presence of sodium sulphite in the electrolyte was not desirable and that it would be better; in order to remove all possible sources of error, if the separation could be effected without its use. Accordingly, ammonium acetate was introduced from the start and the quantity of sodium sulphite was cut down to 0.3 gram and then to 0.2 gram. For precaution's sake the basket electrode, with the major part of the iron on it, was also removed, but it was found that 93 per cent. of the iron had been deposited in two hours, and the rest was found when the electrode was removed at the end of the electrolysis. The surprising result was that the iron and manganese were all out of the solution at the end of four hours. These facts led to arranging the final experiments as follows: Ten cc. of manganese sulphate solution, 10 cc. of a ferric ammonium sulphate solution, 5 cc. of formic acid (sp. gr. 1.06) and 10 cc. of an ammonium acetate solution, after dilution were electrolyzed with a current of 1.1 amperes, with a pressure of 3.9 volts between the electrodes, for five hours. At the end of this time the level of the solution was raised, when no further precipitation took place. The solution was then siphoned off as before, both of the electrodes washed carefully and the iron titrated in the usual manner, while the manganese peroxide was ignited and weighed. The following table shows the close agreement of the results obtained:

Fe present. Gram.	Fe found. Gram.	Mn present. Gram.	Mn found. Gram.	Ammonium acetate.	Formic acid 1.06 sp. gr. cc.	Time. Hours.	Temperature.	N.D_{100} at anode.	N.D_{100} at cathode.	Voltage between electrodes.
0.0996	0.0996	0.0988	0.0990	10 cc. + 10 drops Na_2SO_3.	5	4	ordinary.	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0991	"	5	4	"	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0986	10 cc., no Na_2SO_3.	5	5	"	1.1	1.83	3.9
0.0996	0.0995	0.0988	0.0988	"	5	5	"	1.1	1.83	3.9
0.0996	0.0995	0.0988	0.0990	"	5	5	"	1.1	1.83	3.9
0.0996	0.0994	0.0988	0.0990	"	5	5	"	1.1	1.83	3.9

The deposit of iron had a shining, metallic appearance while the manganese peroxide was black, lustrous, and adherent to the dish.

(2) SEPARATION OF MANGANESE AND ZINC.

A solution of zinc sulphate, containing 0.1 gram of metal in 10 cc., was used. The electrolysis was carried out in a roughened platinum dish serving as anode, while the platinum basket electrode was connected as cathode. It was found that the deposit of zinc showed an extreme tendency to come down in spots upon the cathode, and the basket electrode had to be carefully adjusted so that it was equidistant from the sides of the dish. In this case the addition of ammonium formate exerted beneficial influence on the character of the zinc deposit, the best results being obtained with a solution containing 0.1034 gram of manganese, 0.1000 gram of zinc, 10 cc. of formic acid (sp. gr. 1.06), and 5 cc. of a solution of ammonium formate obtained by neutralizing formic acid (sp. gr. 1.06) with ammonia.

Mn present. Gram.	Mn found. Gram.	Zn present. Gram.	Zn found. Gram.	Time. Hours.	Temperature.	N.D_{100} anode.	N.D_{100} cathode.	Voltage.
0.1034	0.1037	0.1000	0.0998	11	ordinary	1.0	1.66	5.4
0.1034	0.1033	0.1000	0.1001	11½	"	1.0	1.66	5.4
0.1034	0.1036	0.1000	0.1003	11	"	1.0	1.66	5.4

The writer feels justified in claiming that the present investigation has conclusively proved that not only can manganese be easily and accurately determined in the electrolytic way in a formate solution, but that it can also be completely separated in a very simple manner from iron. Indeed, when compared with

any other gravimetric procedure which has been employed for the separation of these metals the electrolytic method is superior in every particular. It is readily executed, it requires less time, and the results afforded by it are most satisfactory. Finally, the separation of manganese from zinc, as described above, is of practical value.

UNIVERSITY OF PENNSYLVANIA.

ON A COLORIMETRIC METHOD FOR THE ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.[1]

BY OSWALD SCHREINER.

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THE estimation of small amounts of phosphates in waters and aqueous extracts of soils and plants is a matter of daily occurrence in the study of field conditions of the soils, of surface and subsurface waters and growing crops, as carried on in the Bureau of Soils, U. S. Dept. of Agriculture. The method first used by Lepierre,[2] also by Jolles and Neurath,[3] and perfected by Woodman and Cayvan,[4] Veitch,[5] and others, consisted in measuring the color developed by phosphates with ammonium molybdate in nitric acid solution against a known solution of phosphate as standard. As silica gives the same coloration with this reagent, its almost unfailing presence in natural waters is a disturbing factor. In the Woodman and Cayvan method, the silica is removed by evaporating once or twice to dryness with nitric acid and heating for two hours in an oven at 100°. The phosphate is then dissolved and separated from the insoluble silica by filtration, and estimated colorimetrically. The need of a more rapid field method induced Prof. F. H. King, Chief of the Division of Soil Management, to direct the investigation of silica and phosphate solutions, which has led to the method here reported.

In the method given in the following pages, the silica is estimated simultaneously with the phosphates. The method is based on the experimental observation that silica solutions will give different intensities of coloration under different conditions, while phosphates give the same coloration under these different con-

[1] Published by permission of the Secretary of Agriculture.
[2] *Bull. Soc. Chim.*, **15**, 1213.
[3] *Monatsh. Chem.*, **19**, 5.
[4] This Journal, **23**, 96.
[5] *Ibid.*, **25**, 169.

ditions. When, as is usually done in the colorimetric estimation of phosphates, the nitric acid and ammonium molybdate solutions are added simultaneously to the silica solution, a certain intensity of color is developed. If, however, the ammonium molybdate reagent is added to the silica solution, and after a period of time the nitric acid, the intensity of color produced by the same amount of silica is far less than in the first case. Experiments have shown that the solution must stand at least one hour with the ammonium molybdate reagent before adding the nitric acid, in order to get the maximum effect. Some color is developed by the ammonium molybdate alone, but this is greatly influenced by the presence of other salts, temperature, etc., but on adding the nitric acid it always comes up to a definite intensity of color, which is approximately only one-half of the color developed when both reagents are added simultaneously. This different coloration of the silica solutions under these conditions is undoubtedly due to the formation of decidedly different silico-molybdates. Phosphates under these two conditions give exactly the same intensity of color.

REAGENTS.

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid* (sp. gr. 1.07).

(3) *Standard Phosphate Solution.*—0.5045 gram of pure, freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram P_2O_5.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting 10 cc. of the above standard phosphate solution to about 80 cc. and then adding 9 cc. of nitric acid (sp. gr. 1.07), and 8 cc. of ammonium molybdate reagent and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5.

COLORIMETER.

The instrument used was similar to the one described and illustrated by Whitson.[1] It consists of a tube of colorless glass, 1 inch by 10 inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution; a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cc. and 100 cc. mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cc. mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

EQUIVALENCE OF THE SILICA COLORATIONS.

To determine the equivalence of the silica colorations, both an alkaline and a neutralized solution of silica were used. The first was prepared by dissolving silica in sufficient solution of sodium hydroxide, made by the action of sodium on water in a platinum dish, to make Na_2SiO_3, and the second by dissolving crystallized Na_2SiO_3 in water and neutralizing with nitric acid. The strength of both solutions was accurately determined gravimetrically and then diluted.

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN BOTH REAGENTS ARE ADDED SIMULTANEOUSLY.

To 50 cc. of the silica solution, 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent were added, and after twenty minutes compared with the standard colorimetric solution in the colorimeter. If the amount of color developed was too great for a safe reading, the solution was diluted and an aliquot part taken and read. The results are given in the following table:

[1] Bulletin 85, Wis. Agr. Expt. Station.

SOLUTION OF $Na_2SiO_3 + 2HNO_3$.

SiO_2 present. mg.	P_2O_5 required to equal color produced by SiO_2. mg.	1 mg. of P_2O_5 equals mg. of SiO_2.
0.0826	0.1580	0.523
0.0826	0.1570	0.526
0.1652	0.3170	0.521
0.3303	0.6140	0.538
0.4139	0.7575	0.546
0.6606	1.2600	0.524
0.8258	1.5000	0.551
0.8258	1.5300	0.540
	SOLUTION OF $SiO_2 + 2NaOH$.	
0.0897	0.1835	0.489
0.3588	0.7220	0.497
0.8970	1.7350	0.517
	Average,	0.525

EQUIVALENCE OF SiO_2 TO P_2O_5 WHEN THE AMMONIUM MOLYBDATE REAGENT IS ADDED ONE HOUR BEFORE THE NITRIC ACID.

To 50 cc. of the silica solution, 4 cc. of the ammonium molybdate reagent were added, and after standing one hour 5 cc. of the nitric acid reagent. After twenty minutes, readings were made as before. The results appear in the following table:

SOLUTION OF $Na_2SiO_3 + 2HNO_3$.

SiO_2 present. mg.	P_2O_5 required to equal color produced by SiO_2. mg.	1 mg. of P_2O_5 equals mg. of SiO_2.
0.1652	0.1490	1.109
0.1652	0.1500	1.101
0.3303	0.3050	1.083
0.3303	0.3075	1.074
0.6606	0.5820	1.135
0.8258	0.7300	1.131
	SOLUTION OF $SiO_2 + 2NaOH$.	
0.0897	0.0900	0.997
0.3588	0.3500	1.025
0.8970	0.9075	0.988
	Average,	1.071

RELATION BETWEEN THE TWO SiO_2 VALUES.

Examining the two silica values for each solution it will become apparent that one is approximately one-half the other. Taking the average value of each type this relation becomes

$$\frac{0.525}{1.071} = 0.49 \text{ or } \frac{1.071}{0.525} = 2.04.$$

The relation of the two silica colorations to each other is, therefore, for all practical purposes, one-half, and this value is used in the following equations for the method.

METHOD FOR THE DETERMINATION OF PHOSPHATES IN THE PRESENCE OF SILICATES.

On the different behavior of silica solutions towards ammonium molybdate under conditions which produce no change in the effect of this reagent on phosphates may be based a method for determining phosphates and silicates when both are present in a solution. There are in solution two unknown quantities; namely, silica (x) and phosphate (y). It has been shown that under a certain condition the silica gives a colorimetric reading which is only one-half as great as under another condition, whereas the phosphates give the same reading under either condition. Hence, when a solution containing both phosphates and silica is subjected to both these conditions, one reading will be obtained under one condition and another reading under the other condition, the differences in the readings being due entirely to the silica. There are, consequently, two equations, and having only two unknown quantities, these can be readily found. These two equations are:

$$(1)\quad x + y = a,$$
$$(2)\quad \tfrac{1}{2}x + y = b,$$

where (x) is the silica reading and (y) the phosphate reading, and (a) the experimental reading obtained under one condition, and (b) the experimental reading obtained under the other condition.

The working of this method is as follows:

Determination of the "a" Reading.—To 50 cc. of the solution add 5 cc. of nitric acid reagent and 4 cc. of ammonium molybdate reagent, and after twenty minutes the colorimetric reading is made. This gives the "a" reading in equation (1).

Determination of the "b" Reading.—To a second portion of 50 cc. of the solution add 4 cc. of ammonium molybdate solution and allow to stand one hour. At the end of this time add 5 cc. of nitric acid reagent and after twenty minutes read in the colorimeter. This gives the "b" reading in equation (2).

From these two readings the true phosphate (y) and silica (x) readings are readily calculated. The silica reading is twice the

difference between the "*a*" and "*b*" readings. To get the silica in milligrams of SiO_2, multiply the reading by 0.00525. The phosphate reading is the difference between the "*a*" reading and the silica reading. To get the phosphate in milligrams of P_2O_5 multiply by 0.01.

APPLICATIONS OF THE METHOD.

The method was tested on known solutions of phosphates in the presence of silicates. The results were as follows:

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2.	P_2O_5.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
3.30	2.00	82.6	50.9	63.4	19.2	3.33	1.92
9.91	20.00	410.0	309.0	202.0	208.0	10.60	20.80

A known phosphate solution containing also the salts usually found in soil solutions or natural waters, silicates, sulphates, bicarbonates, chlorides, and nitrates was prepared and estimated.

p. p. m. present.		Readings for 100 cc.		Readings for		p. p. m. found.	
SiO_2.	P_2O_5.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
3.30	2.00	85.0	52.0	66.0	19.0	3.46	1.90

The method was further tested on some standard salts which had been prepared for field investigations and contained known amounts of phosphates, besides silicates and other salts. These salts were dissolved in water and the solutions estimated. The results were:

	P_2O_5.		p. p. m. of P_2O_5 in solution.		
No.	Present. mg.	Found. mg.	Present.	Found.	p. p. m. of SiO_2.
1.....	0.535	0.536	10.70	10.72	4.18
2.....	0.520	0.532	10.40	10.64	4.65
3.....	0.550	0.522	11.00	10.44	4.26
4.....	0.468	0.471	9.36	9.42	3.70
5.....	0.480	0.451	9.60	9.02	4.04
6.....	0.525	0.506	10.50	10.12	4.26

The phosphates and silica in a well-water were determined. The amount of phosphates in proportion to the silica in this water is quite small, and its determination is, therefore, affected by the unavoidable error of reading. The results obtained with duplicates were as follows:

	Readings for 100 cc.		Readings for		p. p. m.	
No.	"*a*."	"*b*."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
1.....	374.0	192.5	363.0	11.0	19.1	1.1
2.....	370.0	193.0	354.0	16.0	18.7	1.6
				Average,	18.9	1.35

To this same well-water a known amount of phosphate was added and again estimated. The calculated p. p. m. of P_2O_5 is the sum of the p. p. m. added (10), and the average result obtained above (1.35).

	Readings for 100 cc.		Readings for		p. p. m. found.		p. p. m. calculated.	
No.	"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
1....	454	281	346	108	18.2	10.8	18.9	11.35
2....	455	285	340	115	17.9	11.5	18.9	11.35

A soil solution was prepared by washing 100 grams of soil with 500 cc. of water and filtering through a Chamberland filter. The resulting colorless solution was analyzed.

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
203	142	122	81	6.4	8.1

To this same soil solution 5 p. p. m. of P_2O_5 was added and again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	P_2O_5.
254	192	124	130	6.5	13.0	13.1

A plant solution was prepared by washing 20 grams of corn plant with 500 cc. of water. The decolorization of the solution was effected by means of charcoal. The result found was as follows:

Reading for 100 cc.		Reading for		p. p. m.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
450	389	122	328	6.4	32.8

To this same plant solution a known amount of phosphates was added (10 p. p. m.) and the solution again estimated.

Reading for 100 cc.		Reading for		p. p. m. found.		p. p. m. calculated.	
"a."	"b."	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.	SiO_2.	P_2O_5.
547	484	126	421	6.6	42.1	6.4	42.8

It is highly essential for these colorimetric tests that all plant and soil solutions be absolutely colorless.

BUREAU OF SOILS, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE DETERMINATION OF SMALL AMOUNTS OF POTASSIUM IN AQUEOUS SOLUTIONS.[1]

By F. K. Cameron and G. H. Failyer.

Received August 13, 1903.

Some years ago Morrell[2] offered a suggestion by which small quantities of potassium might be estimated. No experimental evidence was presented accompanying this suggestion, and so far as we are aware none has appeared elsewhere. Briefly, the method suggested is to separate the potassium from other bases in the form of the potassium platinic chloride, carefully free from an excess of reagents, take up in water and then add an excess of potassium iodide, when, on standing, a beautiful pink or rose color develops, which gradually deepens to a maximum intensity. By matching the intensity of the color against that which would be developed in a standard solution of known concentration, a measure of the amount of potassium present could be obtained. Qualitative tests indicated that the method could probably be so adapted as to have a great value for a class of work upon which we have been engaged for some time past, and consequently a quantitative examination of the method was undertaken. The color of the solution is due probably to the formation of a double salt of potassium iodide and platinic iodide or chloride, and is but indirectly a method for the detection or estimation of potassium, the same reaction being well known as a delicate one for the detection of small amounts of platinum in solution.

To test the accuracy with which the colors may be compared, a series of solutions of potassium platinic chloride was prepared containing the amounts indicated in the table, expressed in parts of potassium (K) in one million of solution.

Table I.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Calculated.....	0.16	0.31	0.62	0.94	1.40	2.03	2.81
Found.....	0.17	0.33	0.64	0.94	1.40	2.01	2.81

A portion of (*g*) diluted four times was used as a standard for comparison. An inspection of the figures indicates that the method is capable of a high degree of accuracy, the greatest divergence between the calculated and found amounts in this series

[1] Published by permission of the Secretary of Agriculture.

[2] This Journal, **2**, 145 (1880).

being but one part in 50,000,000 parts of solution, although a percentage error slightly greater than 6 per cent. is involved. Nevertheless, considering the magnitude of the quantities involved, the result must be considered quite satisfactory.

A second series of solutions was prepared, the results of which are given in Table II in terms of potassium in 1,000,000 parts of solution.

TABLE II.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Calculated	0.175	0.35	0.70	1.05	1.57	2.28	3.15
Found.....	0.15	0.295	0.65	1.05	1.55	2.28	3.12

In this series, rather larger amounts of potassium iodide and of acid were used than in the first series, the results of which are given in Table I. The agreement between calculated and found results is not quite so happy in this case as in that recorded in Table I. The comparisons were made with much more difficulty, for the reason that the more dilute solutions showed a decided yellow tinge as compared with those of higher concentration. The cause for this will be discussed presently. Nevertheless it was decided to take solution *d* as the standard and make the determinations under the very adverse conditions obtaining. The results, while not as satisfactory as those presented in Table I, yet showed that the method could be used to give fairly satisfactory ideas as to the amounts of potassium in very dilute solutions, providing the separation of the potassium could be effected from other bases which form slightly soluble double chlorides with platinum. A seaching trial was then given the method, using solutions of potassium of known and of unknown strength, solutions of pure salt, and those containing the salts of other bases as well. Certain details of manipulation were found advisable and in some cases even essential to the successful use of the method, so that we feel justified in stating them here at some length.

If the solution under examination contain ammonium salts or organic matter, these must be removed, as the ammonia would precipitate a slightly soluble double chloride with platinic chloride, and the organic matter would color the solution and thus interfere with the reading. To effect their removal, the solution is evaporated with a few drops of sulphuric acid; enough to unite with all the bases presented. When dry, the residue is heated over a

naked flame, at first gently, then strongly. After cooling, a few drops of hydrochloric acid and of platinic chloride solution are added. The amount of these will depend upon the amount of residue. The platinum must, of course, be added in excess. This may be judged fairly well by observing whether the solution is yellow after any precipitate has settled out. The platinic chloride solution is run around over that portion of the dish containing the residue, a few drops of water, free from ammonia, being added if necessary. It is again evaporated to dryness on a water- or steam-bath. All operations after the ignition with sulphuric acid must be so conducted that no ammonia has access to the solutions. In the absence of ammonium salts and organic matter, the use of sulphuric acid may be dispensed with, the platinic chloride and a very small amount of hydrochloric acid being added to the original solution, one evaporation sufficing. When dry, or in the condition of a very stiff paste (but in the small quantities usually involved, the residue will be a thin layer over the bottom of the dish and may be carried to dryness) the dish is cooled, and the potassium platinic chloride washed, as described below. An excess of platinic chloride must have been used to throw down all the potassium, and as the color to be finally read is a measure of the platinum then present, it is obvious that all the forms of platinum other than potassium platinic chloride must be removed. To effect this with the solution of as little as possible of the precipitated potassium platinic chloride, we have used in our earlier work alcohol nearly saturated with this salt. Such a solution will only slowly dissolve the precipitate, and should a little of the alcohol evaporate, there will be no separation of potassium platinic chloride. We have washed and filtered through asbestos, resting on Witt or Hirsch plates fitted into carbon filters, using gentle suction. By this means the washing is done rapidly and there is a minimum evaporation of the alcohol containing potassium platinic chloride, if the suction be shut off as soon as the alcohol has passed through. The final washing is with ordinary strong alcohol, running through four or five small portions to remove the alcohol saturated with potassium platinic chloride. There is apparently a balancing of errors here, so that we have looked into this point very carefully, and have found that, while potassium platinic chloride has an easily measurable solubility in alcohol if the two are left in contact

sufficiently long, yet this solubility is so small and takes place so slowly that in repeated experiments the alcohol used in washing the precipitate, as we have described above, would have no appreciable effect on the potassium platinic chloride in the precipitate. We have, therefore, abandoned the alcoholic solution of potassium platinic chloride, and wash the precipitate at once with six or eight small portions of 95 per cent. alcohol, being careful to remove each portion as completely as possible before the next one is added.

Should the alcohol have crept up the sides of the dish or funnel, carrying with it platinic chloride, any deposit of the latter must be carefully removed. After the washing is completed, the potassium platinic chloride is dissolved and washed through the asbestos with hot water into a flask, allowed to cool, a drop of concentrated hydrochloric acid is added, and then a solution containing potassium iodide until there is present a decided excess of this reagent. To secure the desirable tint of red, the color should be developed in a strong solution, and any necessary dilution be made some time (about four or more hours) later. It is, therefore, better not to dilute further than necessary in washing the potassium platinic chloride out of the filter before adding the hydrochloric acid and the potassium iodide.

In order to compare the test solutions with a standard, the procedure adopted is to place the solution under examination in a glass cylinder with a bottom ground flat and polished, such as the well-known apparatus used for determining ammonia by the Nessler method. A second cylinder with precisely the same dimensions as the first, but made with a side arm at the bottom, contains the standard solution. Both cylinders are clamped into position parallel with each other, within a box or camera[1] fitted with mirrors, so that a beam of light can be thrown through the cylinders from above and the images of their cross-sections be seen on a lower mirror arranged at a convenient angle. The bottoms of the cylinders rest upon a shelf with orifices so arranged that no light from the upper mirror falls upon the lower mirror other than that which passes through the columns of liquid contained in the cylinders. By means of the side arm and rubber tubing, the cylinder containing the standard solution

[1] A convenient form of instrument for this purpose is that described by Whitson, Bull. No. 85, Wis. Agr. Expt. Station.

is connected with a movable reservoir outside the camera which can be raised or lowered at will, thus regulating the depth of the standard solution within the cylinder. This depth of the standard solution is adjusted until the intensity of color of the two images is the same. The cylinder containing the standard solution is fitted with a scale, for which purpose a strip of cross-section paper pasted along the side answers very well, and is then calibrated on the assumption that when the images given in the camera by two solutions contained in identical cylinders are the same, the concentrations of the two solutions are inversely proportional to the height of the two columns of liquid. This assumption is not free from objections on theoretical grounds, but has been found entirely justifiable in the case here considered, as the result of long and repeated series of experiments. It carries with it as a necessary consequence the further assumption that the color produced by the solution in a standard cylinder is dependent only upon the amount of coloring-matter present and not upon the amount of water, a point of importance, since it enables one to avoid having always to dilute the test solution to mark in the cylinder, which procedure might sometimes be undesirable, as the following pages will show.

The substance which causes the red color in these solutions has not been determined. An inspection of the literature describing the double halides of platinum and potassium failed to give any positive information, and we have not felt justified at the present time in extending our investigation so as to definitely decide this question. In order to obtain some idea as to the proportions of the reagents necessary to the use of the method, a series of experiments was made.

For this purpose ten solutions were prepared, each containing the same amount of potassium platinic chloride, this salt being used instead of platinic chloride, since it is possible to weigh the desired amount of platinum more accurately with the former than with the latter salt. And since there was no purpose of studying the relation of the solution to solid phases, they were in all cases, after the addition of potassium iodide, brought to a volume of about 50 cc., enough to have no solid phase present at the beginning of the experiments. In each solution there was brought the amounts of potassium iodide indicated in the table. The ratios are approximate only.

TABLE III.

	Weight of K_2PtCl_6 taken. mg.	Weight of KI required to form K_2PtI_6. mg.	Weight of KI used. mg.	Ratio of KI used to that required to form K_2PtI_6.	Remarks.
a	3.105	6.26	1.093	0.2 : 1	Pink, soon darkened, the pink color disappeared and a black residue separated out.
b	3.105	6.26	2.395	0.33 : 1	
c	3.105	6.26	3.975	0.66 : 1	
d	3.105	6.26	7.95	1.25 : 1	Pink; turned dark after a time; black residue.
e	3.105	6.26	15.9	2.5 : 1	Pink; shining metallic film.
f	3.105	6.26	31.8	5 : 1	Pink.
g	3.105	6.26	47.7	7.5 : 1	"
h	3.105	6.26	63.6	10 : 1	"
i	3.105	6.26	79.5	12.5 : 1	"
k	3.105	6.26	95.4	15 : 1	"

Solutions (*e*) to (*k*) inclusive, were of a satisfactory pink or red color, which apparently remained permanent for seven days. A very careful examination with starch paste at the end of that time yielded a faint reaction for iodine in some of the solutions, and the experiments were then abandoned. The results showed that it would be desirable to use about five times the amount of potassium iodide required by calculation to form the salt of the formula K_2PtI_6, but that no obvious advantage was produced by having a larger excess present.

It early developed in the work that the color of the solution did not reach a maximum until some hours after the reagents were brought together, and that the speed of the reaction was greatly augmented by the presence of a little free acid.[1] Therefore, a series of solutions were prepared from one containing about two parts per million of potassium to which the two drops of the acids indicated were added, the acids being taken from the ordinary reagent bottles of the laboratory shelf and marked "concentrated." Readings were made in the times indicated, a solution whose strength was known approximately (but not accurately), and in which the rose color had been developed twenty-four hours previously being used as the standard.

[1] It is obvious that the amount of free acid permissible is very small, otherwise iodine would be liberated.

TABLE IV.

Acid used.	After 1 hour.	After 1½ hours.	After 4½ hours.	After 22 hours.
No acid	Trace	Trace	Lost	....
	Trace	Trace	0.20	0.33
Hydrochloric	1.33	1.53	1.93	1.93
	1.33	1.56	1.86	1.93
Acetic	0.46	1.13	1.83	1.86
	0.53	1.13	1.80	1.86
Nitric	1.33	1.53	1.73	1.86
	1.26	1.53	1.80	1.86
Sulphuric	1.33	1.56	1.86	1.93
	1.33	1.60	1.93	2.00

The results of these experiments, with many others which it is not worth while recording here, have led us to the procedure of adding one drop of strong hydrochloric acid to the solution before adding potassium iodide and then waiting at least four hours for a full development of the color before reading in the colorimeter. It has, moreover, been found desirable to make all dilutions, even of strongly colored solutions, at least one hour before readings are taken. The pink color can be brought to its maximum intensity within a comparatively few minutes, by warming the solution, and this procedure we occasionally follow rather than the one just advised. But unless great care has been taken to eliminate all traces of alcohol before dissolving the precipitate from the alcohol, warming the solution is apt to produce a yellowish or brownish tinge in the pink color, rendering its comparison with the standard much more difficult, if not impossible.

To test the efficiency of the method when other bases than potassium are present, a series of experiments were made, the results of which are given in the following table. Since becoming more expert in handling the method, we generally obtain more satisfactory results than these, but we give them here as actually obtained when working out the method, as indicating the probable order of accuracy to be expected by one having no previous experience with the method. Except as otherwise indicated, all results are expressed in this paper as parts per million of solution.

TABLE V.

Calculated.	Found.	Remarks.
50	52.7	50 parts Na, 50 parts Mg, and 50 parts Ca per 1,000,000 parts solution, also present.
	48.0	
	48.0	
	53.5	
	52.7	

20	19.8 19.4 20.2 21.0 19.4	20 parts Na, 20 parts Mg, and 20 parts Ca per 1,000,000 parts solution, also present.
5	6.4 6.4 6.9 6.0	5 parts Na, 5 parts Mg, and 5 parts Ca per 1,000,000 parts solution, also present.
20	20.2 20.1 20.1 20.0	No other base present.
	12 2 11.9	Aqueous extract of a soil.
	11.2 11.5	" " " "
	30.6 30.2	" " " "
	20.3 24.3	" " " "
	9.7 9.3	" " " "
	12.7 13.8	" " " "
	58.0 61.0	" " " "
	13.0 14.5	" " " "

To test the method still further, the three solutions cited above and containing sodium, magnesium and calcium, as well as potassium, were further examined, comparisons being made with solutions containing 2 parts and 3 parts per million of potassium, respectively, and the potassium being estimated gravimetrically as well, according to the well-known method of weighing the precipitated potassium platinic chloride, large volumes of the solutions being taken for this purpose. The results have been tabulated as follows:

TABLE VI.

Calculated.	Gravimetric.	Standard 2 parts per million.	Standard 3 parts per million.
5	4.7	5.2	5.3
	4.2	5.2	5.3
20	..	20.5	20.4
	22.5	20.5	20.4
50	50.7	49.0	48.8
	...	48.5	48.8

These results show that the method can be regarded as fairly satisfactory, even when relatively large proportions of other bases are present. The method has been used successfully with solutions containing originally as much as 400 parts per million of potassium, by properly diluting. But we do not advise its application to solutions containing more than 50 parts per million of this base, at most, unless the volume at command is so small as to prevent obtaining a sufficiently large precipitate to weigh satisfactorily. The method seems to be most satisfactory when applied to solutions containing from 1 to 10 parts per million of the base, and on the whole the most satisfactory concentration for the standard we have found to be 2 parts per million. For solutions containing less than 2 parts per million, the method has been found quite satisfactory, if care be exercised. The weak point of the method is obviously the handling and washing of the precipitate of potassium platinic chloride, and the smaller this is, the greater the difficulty becomes, and in consequence the greater the care which must be exercised.

Attention has been called above to the fact that the solutions to which the potassium iodide had been added were sometimes brownish or yellowish, thus rendering their comparison with others impossible or at least unsatisfactory. The cause of this escaped us for some time. But the fact that the pink color is not produced when potassium iodide is added to an alcoholic solution of platinic chloride, led Mr. J. F. Breazeale, of this laboratory, to suspect that small quantities of alcohol left in the filter, when washing the potassium platinic chloride free from other salts, and subsequently brought into the solution on the addition of hot water, might be responsible for the trouble. Experiments have amply verified this view. The addition of small amounts of alcohol to aqueous solutions in which the pink color had already been developed, invariably turned them yellow. This change to yellow was found to take place more rapidly in the sunlight. If the solution containing the platinum salt and to which the potassium iodide has been added together with a little alcohol, be heated, the pink color first appears, develops very rapidly, but always with a yellowish or brownish tinge, and after a few minutes turns to a clear yellow. The presence of a free acid retards the development of the yellow color, and if this color be desired in the first place,

acid should preferably not be added. The yellow color is not so intense as the pink we have been describing, but much stronger than the yellow obtained from an equivalent amount of platinum combined as platinic chloride. We have, therefore, examined it with a view to its application for the quantitative estimation of platinum and indirectly of potassium.

A series of solutions containing known amounts of potassium was prepared. Mr. Breazeale and Mr. J. G. Smith, of this laboratory, were requested to read them independently against standards prepared by themselves, developing first the pink color and then subsequently developing the yellow color in the identical solutions which had just been read, and then re-reading. The results obtained follow under the headings B and S.

TABLE VII.

	Found by B.		Found by S.	
Calculated.	Pink.	Yellow.	Pink.	Yellow.
0.75	0.80	0.84	0.70	0.80
1.25	1.20	1.26	1.10	1.30
1.25	1.20	1.34	1.30	1.30
2.50	2.48	2.62	2.40	2.40
2.50	2.48	2.52	2.40	2.40
3.75	4.44	3.40	4.00	3.80
5.00	...	5.30	...	...
5.00	...	5.10	...	...
10.00	...	10.00	...	...
10.00	..	10.00	...	...

A series of water extracts of soils was then prepared, in which other bases than potassium would also be present, and they were compared by means of both the pink and the yellow color methods. The results follow:

TABLE VIII.

Pink.	Yellow.
2.4	2.8
12.5	13.5
4.2	4.4
17.7	17.1
5.7	5.4
18.8	18.9
23.9	26.2
4.4	4.7

From the results it would appear that the yellowish color can be used as well as the pink over the range of concentrations indicated

in these tables. The yellow color is probably somewhat easier to "match" than the pink, and its use is advised when the higher concentrations are concerned. It is also of considerable advantage in that it affords a ready check upon the determination by the pink color, a matter of importance when such small amounts of unknown solutions are available as to preclude duplicate determinations. The yellow color is not so deep or strong, however, as the pink, and for this reason the latter is much more advantageous than the former, when high dilutions are concerned.

From what has been presented in this paper, it is evident that we have here a very sensitive method, susceptible of a high degree of accuracy, for determining quantitatively minute quantities of potassium. No unusual apparatus or skill is required for its manipulation. But it will only yield satisfactory results when care is exercised, and especially in the handling and washing of the small precipitate of potassium platinic chloride. The limit of dilution to which the method is applicable is probably much higher than the figures given here would indicate, but we have not attempted to determine this limit, and are not prepared to make a more definite statement concerning it.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE ESTIMATION OF TITANIUM.

BY J. WATSON BAIN.

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OF THE many elements which present themselves for determination to the metallurgical chemist of to-day, there are a select few which have won for themselves a reputation based upon the tediousness or the difficulty of the preliminary separation from other constituents which may be present. In this class of unenviable reputation we may place the element titanium for, although its determination presents no difficulties to the experienced chemist with time at his disposal, his less fortunate brother, at the same task in the rush of a works laboratory, is apt to find that either speed or accuracy must be sacrificed in answer to the demands made on him.

For three-quarters of a century the estimation of this element

in all pure solutions involved six or eight hours' boiling, an operation which had often to be repeated, or else a tedious treatment with ammonium sulphide, until Gooch[1] discovered that titanium could be precipitated quantitatively in a convenient form by a few minutes' boiling, and Blair[2] added to this a modification which permitted a much more rapid separation from iron than heretofore. Thus the determination became comparatively easy, but nevertheless under the pressure of heavy work and insufficient time, the demand for a shorter method has become noticeable and in response several modified processes have appeared in the chemical literature of the day. To inquire into the accuracy of these was the first object of the following investigation. At the same time it has not been considered necessary to confine the attention to speed, and hence some experiments have been incorporated simply because they have a bearing upon the estimation of titanium in general. In the foregoing statements, there has been a reservation regarding Weller's[3] excellent colorimetric method; it is rapid and accurate, but unfortunately is only adapted for the estimation of small quantities of titanium.

To the chemist engaged in the analysis of minerals and rocks, the separation of titanium from some of the rarer elements such as zirconium or vanadium is a matter demanding attention, but to the metallurgical chemist who meets these more uncommon elements either rarely or in minute quantities, the elimination of iron, aluminum and phosphorus is usually the only problem to be considered. For this reason, the behavior of these last three elements, with the one under consideration, has been the object of this study. At the same time it will readily be seen that all our present knowledge can be directly employed in the final stages of any of the methods investigated.

Without referring in detail to the modifications of the older processes, descriptions of which are to be found in modern chemical or metallurgical journals, it is proposed to discuss the merits of three methods which are apparently new in principle. In the following pages, these have been designated for convenience by the author's name; if any injustice has been done, the writer begs to offer his apologies.

[1] Gooch: Bull. 27, U. S. Geol. Survey, p. 16; *Proc. Am. Acad. Arts Sci., n. s.*, **13**, 435; *Chem. News*, **72**, 55, 68.

[2] Blair's "Analysis of Iron and Steel," 4th edition, p. 179.

[3] *Ber. d. chem. Ges.*, **15**, 2593.

For the purpose of the investigation a solution of pure titanium dioxide was necessary, and this was prepared from rutile by Wöhler's[1] method. The mineral at hand, however, was very impure and only a small yield of potassium fluotitanite was obtained. The process was therefore modified by preparing, according to the directions of Streit and Franz,[2] a quantity of fairly pure titanium dioxide, which was then converted into the fluotitanate and finally by the action of strong sulphuric acid into titanium sulphate. Incidentally it may be mentioned that this modification is much more convenient for the preparation of considerable quantities of pure potassium fluotitanate, but Merz's[3] process, a description of which was found after the preparation had been made, appears to be the best. After the removal of the excess of sulphuric acid, the pasty mass of potassium and titanium sulphates was treated with water, solution being accelerated by warming to 70° C. and agitating with a blast of air. After suitable dilution, ammonia was added to weighed quantities of this standard solution till alkaline, followed by acetic acid in decided excess[4] and the titanium dioxide, precipitated by boiling for two or three minutes, was filtered off, thoroughly washed, and ignited to constant weight.

Weight of solution. Grams.	TiO_2 found. Gram.	TiO_2 in 25 grams standard solution. Gram.
27.8603	0.2611	0.2343
27.8518	0.2624	0.2355
27.8384	0.2624	0.2356
27.8540	0.2620	0.2351
	Mean value =	0.2351

Every precaution was taken to make these results as accurate as possible, and it is believed that the mean approximates very closely to the true value.

BASKERVILLE'S METHOD.

The detailed description[5] may be briefly summarized as follows: The material is fused with potassium bisulphate and the mass dissolved in water, ammonia is added till alkaline, and the hy-

[1] Wöhler: *Am. Chem. Pharm.*, **74**, 212.
[2] Streit and Franz: *J. prakt. Chem.*, **108**, 65; *Ztschr. Chem.* [2], **6**, 256.
[3] Merz: *J. prakt. Chem.*, **99**, 157.
[4] Gooch: *Loc. cit.*
[5] Baskerville: *J. Soc. Chem. Ind.*, **19**, 419; also this Journal, **16**, 427.

droxides are filtered off, washed and redissolved in hydrochloric acid. Ammonia is then added till the solution reaches the so-called neutral point and the volume is brought to about 100 cc., sulphur dioxide is passed in to saturation, and three minutes' boiling precipitates the titanium dioxide. If the latter be not perfectly white, the process is repeated. One point deserves attention. After dissolving the hydroxide precipitated by ammonia in 15 cc. of dilute hydrochloric acid, to quote the original: "Very dilute ammonium hydroxide is now added slowly to neutralize the acid. When a slight permanent precipitate is obtained, 1 per cent. hydrochloric acid is added drop by drop, boiling after each addition until the solution just becomes clear; the total amount of liquid should not be more than 100 cc." The writer has endeavored to follow out these directions in a number of cases, but has always failed to secure the desired effect. The 1 per cent. hydrochloric acid will not dissolve the precipitate even after a large quantity has been added, and this result could be predicted from a knowledge of the behavior of salts of titanium in solution. For example, a solution containing titanium and ferric chlorides, after being nearly neutralized, but while still free from the faintest trace of a precipitate, becomes turbid on boiling, and the metatitanic acid thus precipitated is apparently quite unattacked by 1 per cent. hydrochloric acid even in considerable amount. The following modification was, therefore, adopted in the experiments to be described: Dilute ammonia was added to the solution of the chlorides until a faint permanent precipitate was formed which was just redissolved with a drop or two of dilute hydrochloric acid, or in other words, the solution was treated exactly as though a basic acetate separation were to be made. In all other details the method was carefully followed, notwithstanding the fact that slight alterations suggested themselves from time to time.

The Separation of Titanium from Iron.—Iron is almost invariably present in the materials in which titanium is to be estimated, and consequently this separation was the first to be studied. To a weighed quantity of the standard solution, 0.5 gram iron as $Fe_2(SO_4)_3$ was added, then ammonia to alkalinity, followed by acetic acid in slight excess. The latter reagent was employed because it was thought that traces of titanium, which might have escaped precipitation with ammonia alone, would then be thrown

down, although no direct experiments were made to settle the point. It will be remembered, however, that Gooch found advantageous the presence of a distinct excess of acetic acid when estimating titanium in a pure solution. The hydroxides, after washing till the sulphates were almost entirely removed, were dissolved in dilute hydrochloric acid, and the solution neutralized with ammonia till a faint permanent precipitate was formed, which was redissolved in a drop or two of dilute acid. Sulphur dioxide was then passed in to saturation; in the course of a few minutes a white precipitate usually began to form. After boiling for five minutes the hydrated titanium dioxide separated out in flocks, and the supernatant liquid showed the characteristic, faint greenish tinge of solutions containing ferrous chloride. The precipitate was filtered off, washed with hot water, and ignited to constant weight.

	Weight of solution. Grams.	TiO_2 found. (I) Gram.	TiO_2 by standard. Gram.	Error.
(3)	6.639	0.0662	0.0624	0.0038+
(4)	7.720	0 0707	0.0684	0.0023+
(5)	11.169	0.1136	0.1050	0.0086+
(6)	11.167	0.1138	0.1050	0.0088+
(7)	11.085	not	0.1045	.....
(8)	11.087	weighed.	0.1045	.....
(9)	11.137	0.1062	0.1049	0.0013+
(10)	11.140	0.1108	0.1049	0.0059+

As will readily be understood, the amount of iron thrown down with the titanium dioxide depends on the manner in which the solution is neutralized. Where this was carried out with the greatest care, the solution being only gently warmed till completely reduced, as was the case in (4) and (9), the results approximated to the truth with exactness sufficient, at least, for technical work; this accuracy is, however, due to a balancing of errors, as will be shown later on. Numbers (7) and (8) were treated with ammonia till a faint precipitate remained persistently; on heating, the turbidity appeared to become less, and before 100° C. had been reached, the burner was removed and sulphur dioxide passed in. The first few bubbles produced a reddish white precipitate; after saturation and boiling, this turned brownish red in color and evidently contained a considerable quantity of iron. This became more apparent on ignition and no weighings were made at this stage. The purity of the titanium dioxide may be

judged roughly from its color after precipitation; if snow-white, iron is almost entirely absent, but when contaminated with that element, a reddish or pinkish tinge is noticeable, the more pronounced the greater the impurity. The same effects may also be noted in the ignited precipitate. The precipitates were dissolved, if very impure, by treatment with potassium bisulphate, or otherwise by fusion with sodium carbonate and solution in concentrated sulphuric acid; in the former case, care was taken to remove from the solution subsequently obtained, the platinum from the crucible. The entire process as described above was then repeated, yielding the following results:

	Weight of solution. Grams.	TiO_2 found. (II) Gram.	TiO_2 by standard. Gram.	Error.
(3)	6.639	0.0580	0.0624	0.0044—
(4)	7.270	0.0651	0.0684	0.0033—
(5)	11.169	0.1032	0.1050	0.0018—
(6)	11.167	0.1031	0.1050	0.0019—
(7)	11.085	0.1056	0.1045	0.0011+
(8)	11.087	0.1027	0.1045	0.0018—
(9)	11.137	0.1012	0.1049	0.0037—
(10)	11.140	0.1025	0.1049	0.0024—

Some of these precipitates still retained iron and the results should be corrected before criticism is made; determinations were not carried out in (3) and (4), and in (6), which was accidentally lost after estimating the platinum, iron was also present, and the error is greater than —0.0019 gram.

	TiO_2 found. (II) Gram.	Fe_2O_3 therein. Gram.	TiO_2-Fe_2O_3. Gram.	TiO_2 by standard. Gram.	Error.
(5)	0.1032	0.0027	0.1005	0.1050	0.0045—
(7)	0.1056	0.0015	0.1041	0.1045	0.0004—
(8)	0.1027	0.0001	0.1026	0.1045	0.0019—
(9)	0.1012	0.0002	0.1010	0.1049	0.0039—
(10)	0.1025	0.0000	0.1025	0.1049	0.0024—

From these results, some interesting deductions can be drawn. In the first place, it will be remembered that in (7) and (8) so much iron was thrown down in the first precipitation that the weighing was omitted, and it will be seen that in these two instances the final errors are the lowest of all. One might therefore purposely produce a similar condition with a view of attaining greater accuracy. Again it will be observed that, presumably, after experience in the operation had been gained, the second

precipitation yielded titanium dioxide practically free from iron, as shown in (8), (9), and (10), but apparently always at the expense of a loss in the titanium. Omitting (7) as exceptional, the average loss in the element under estimation is 3 per cent. In most of the filtrates, colorimetric estimations were made of the titanium which remained in solution, but no light was thrown upon the question as to the conditions under which the greatest loss took place. The amounts found varied from traces to 1.5 milligrams.

From the standpoint of technical work, the uncorrected results of the second precipitation are worth noting. The errors here can be overlooked in view of the fact that titanium is not bought and sold at so much per unit, and if a small amount of iron remain in the final precipitate it serves but to balance the loss in the element estimated. An interesting case may be cited at this point as an instance of the curiously exact results which may sometimes be obtained in cases in which all precautions are not taken. The impure titanium dioxide obtained in the first precipitation in (5) and (6) was fused with potassium bisulphate, and inadvertently the second precipitation was made without removing the platinum by hydrogen sulphide as usual. After weighing, the precipitates were fused again with potassium bisulphate in porcelain and the platinum and iron estimated; in (6), an accident prevented the completion of this operation after the platinum, which amounted to 0.0019 gram, had been determined.

	TiO_2 by standard. Gram.	TiO_2 found. Gram.	TiO_2 found less impurities. Gram.	
(5)	0.1050	0.1059	0.1005	
(6)	0.1050	0.1050	0.1031	(less Pt only.)

It may be remarked at this point that Baskerville makes no provision for the removal of the platinum which is always present after a fusion with potassium bisulphate and that this precaution may only be neglected in the hope that a balancing of errors will ensue.

The Separation of Titanium and Aluminum.—To weighed quantities of the standard solution were added 1.75-gram portions of alum, equivalent to 0.1877 gram alumina. The hydroxides were precipitated with ammonia, washed, redissolved in hydrochloric acid, the solution neutralized with ammonia and after dilution to 100 cc., boiled for three minutes.

	Weight of solution. Grams.	TiO_2 found. (I) Gram.	TiO_2 by standard. Gram.	Error.
(11)	6.105	0.0575	0.0574	0.0001+
(12)	6.215	0.0592	0.0584	0.0008+
(13)	11.185	0.1076	0.1052	0.0024+
(14)	11.177	0.1044	0.1052	0.0008—

To ascertain what quantity of alumina still remained in these precipitates, recourse was had to Gooch's method which assured the separation of the small amount retained without the risk of losing any of the titanium. The precipitates were accordingly fused with pure sodium carbonate, leached with water, re-fused with sodium carbonate and treated with concentrated sulphuric acid until complete solution took place. The remaining steps of the process were carried out as usual, the titanium being precipitated from a solution strongly acidified with acetic acid. After this treatment the following results were obtained:

	Weight of solution. Grams.	TiO_2 found. (II) Gram.	TiO_2 by standard. Gram.	Error.
(11)	6.105	.....	0.0574	.....
(12)	6.215	0.0582	0.0584	0.0002—
(13)	11.185	0.1044	0.1052	0.0008—
(14)	11.177	0.1036	0.1052	0.0016—

It will thus be seen that with the smaller amounts of titanium in (11) and (12), the separation from a fairly large quantity of alumina is remarkably sharp for one precipitation, much more so than in any of the cases given by Gooch as examples of the efficiency of his method. Even the larger quantities of titanium dioxide retain only trifling quantities of alumina, and it is easy to arrange for their removal. Having regard to the observation which has been made in the course of this study that minute but determinable quantities of titanium are almost invariably to be found in the filtrates from Baskerville's method, but very much smaller quantities or only traces in the filtrates from Gooch's method, and desiring to avoid loss as far as possible, the following would appear to be the best method of purification. The impure titanium dioxide is fused with pure sodium carbonate, leached with water, re-fused with sodium carbonate, and the melt dissolved in concentrated sulphuric acid by gentle warming; the titanium dioxide in this solution is then precipitated according to Gooch's directions.

The Separation of Titanium and Phosphorus.—The fact that

titanium phosphate is almost insoluble in dilute hydrochloric acid would lead to the prediction that a separation of these elements under the conditions laid down by Baskerville could not be expected, and consequently no experiments were made in this direction. A little later, however, some evidence bearing on this point will be presented.

The Separation of Titanium from Iron, Aluminum and Phosphorus.—Since these elements present themselves in varying quantities in nearly every instance in which titanium is to be estimated, an inquiry was made as to their behavior when all are present at the same time. The following quantities were taken:

Standard solution of TiO_2	10 cc.
50 cc. solution of $Fe_2(SO_4)_3$	= 0.5000 gram Fe.
0.9294 gram alum	= 0.1000 gram Al_2O_3.
0.1000 gram sodium phosphate	= 0.0200 gram P_2O_5.

After diluting to 200 cc., ammonia and acetic acid were added as already described and the precipitate, after washing, was redissolved in hydrochloric acid, 1:1. Some flocks of titanium phosphate, which obstinately resisted attack, were digested with concentrated hydrochloric acid, in which they finally dissolved. The solution was then neutralized and boiled for five minutes after saturating with sulphur dioxide. The color of the precipitated titanium dioxide varied from almost pure white to gray or brownish, and a considerable amount of impurity was present in each case, as may be seen from the following:

	Weight of solution. Grams.	TiO_2 found. (I) Gram.	TiO_2 by standard. Gram.	Error.
(15)	11.180	0.1464	0.1052	0.0412+
(16)	11.174	0.1274	0.1052	0.0222+
(17)	11.210	0.1316	0.1055	0.0261+
(18)	11.209	0.1256	0.1055	0.0201+

The precipitates were accordingly fused with sodium carbonate, dissolved by gently warming with strong sulphuric acid—the solution in this and similar instances was often incomplete, necessitating filtration and re-fusion—and after suitable dilution, precipitated with ammonia. Finally, a reprecipitation was made in the neutralized chloride solution, as described above, yielding the results stated below.

	Weight of solution. Grams.	TiO_2 found. (II) Gram.	TiO_2 by standard. Gram.	Error.
(15)	11.180	0.1105	0.1052	0.0053+
(16)	11.174	0.1154	0.1052	0.0102+
(17)	11.210	0.1203	0.1055	0.0148+
(18)	11.209	0.1127	0.1055	0.0072+

Thus a double precipitation in a neutralized chloride solution fails to effect the complete separation of the titanium from the elements associated with it in this instance. It remained, then, to discover what amount of pure titanium dioxide was present in these precipitates and whether any one element was responsible for the magnitude of the error.

The precipitates were fused with sodium carbonate, leached with water, and re-fused with the same material. The mass was then dissolved in concentrated sulphuric acid with the aid of gentle heat and after pouring into water, in (15) and (16) hydrogen sulphide was passed in to saturation in order to discover whether appreciable amounts of platinum were present, an element which is well known to contaminate titanium dioxide, if present during its precipitation; only traces were found and the question was considered as settled. After carefully adding ammonia till just alkaline, a quantity of dilute sulphuric acid equivalent to 2.5 grams of the pure acid was added, then 20 grams sodium acetate and sufficient acetic acid to make 11 per cent. absolute acid in the solution. If ferric iron could be detected, sulphur dioxide was passed in at an appropriate stage. After boiling for three minutes and digesting on the water-bath for half an hour, the titanium dioxide was filtered off and washed with 7 per cent. acetic acid.

	Weight of solution. Grams.	TiO_2 found. (III) Gram.	TiO_2 by standard. Gram.	Error.
(15)	11.180	0.0948	0.1052	0.0104—
(16)	11.174	0.0976	0.1052	0.0076—
(17)	11.210	0.1010	0.1055	0.0045—
(18)	11.209	0.0968	0.1055	0.0087—

These precipitates still retained trifling quantities of iron.

With regard to the disturbing factor, some evidence may be given. After fusing 0.1105 gram of impure titanium dioxide obtained in the second precipitation in neutralized chloride solution in (15), with sodium carbonate and leaching with water, the phosphorus was determined in the extract and found to be equivalent to 0.0123 gram phosphorus pentoxide; the final precipitate from the acetic acid solution in the same instance weighed 0.0948 gram. $0.1105 - 0.0123 = 0.0982$ gram impure $TiO_2 - P_2O_5$.

Any alumina would, of course, have been removed with the

phosphorus, but, judging from the separation previously studied, there was now but a minute amount present and the difference 0.0982 — 0.0948 = 0.0034 gram represents in all probability the iron eliminated, the latter clearly being indicated in the waste liquors by qualitative tests. Similar treatment of the titanium dioxide obtained in the second precipitation in the neutralized chloride solution in (17) and (18) revealed the fact that phosphorus constitutes almost the entire impurity, with a small quantity of iron as its associate. In the filtrates from the neutralized chloride separations, titanium was found regularly and in amounts varying from traces to 3 or even 4 milligrams.

While, obviously, the attempted separation is rendered practically valueless by such serious losses in titanium, it must not be forgotten that the object was to subject the method to a severe test. The presence of the titanium phosphate no doubt made difficult the adjustment of the acidity of the solution, since it would be precipitated by the ammonia in neutralizing, and, dissolving very slowly or not at all, would induce the belief that but little free acid remained. Consequently the removal of the phosphorus and at the same time the remaining aluminum, after the first precipitation, by fusing with sodium carbonate and leaching with water should be undertaken, after which the problem resolves itself into the separation of iron and titanium, which has already been studied. Also, if a fusion with potassium bisulphate has been made at any stage, the platinum, which is invariably present, should be removed, preferably in hot sulphuric acid solution, before the final precipitation.

Brakes[1] has modified Baskerville's method by replacing the potassium bisulphate, used in the preliminary fusion, by sodium and potassium carbonates. The melt is dissolved in dilute hydrochloric acid, and, after filtering, the titanium is precipitated in the neutralized chloride solution as usual. Some results are given showing that closely agreeing figures may be obtained, but one cannot gather what degree of accuracy is reached.

ARNOLD'S METHOD.

Blair's statement that "when a solution of ferric chloride containing titanic and phosphoric acids is evaporated to dryness, a compound of titanic acid, phosphoric acid and ferric oxide is

[1] Brakes: *J. Soc. Chem. Ind.*, **18**, 1097.

formed, completely insoluble in dilute hydrochloric acid,"[1] suggests a method of removing, with comparative ease and certainty, the large amount of iron and alumina which have usually to be separated from titanium in analytical work. Morgan[2] and Arnold[3] have published methods founded upon this observation, and an inquiry was made as to their value. Waterhouse[4] indeed states that the results may not be accurate, but presents no evidence in support of his assertion.

The descriptions may be abbreviated as follows: The finely ground ore, to which has been added 1 gram of ammonium phosphate, is treated with concentrated hydrochloric acid, the solution evaporated to dryness and baked for some time, then treated with dilute hydrochloric acid and the residue filtered off, the filtrate being discarded. By fusing with sodium carbonate and leaching with water, the phosphorus and most of the silica and alumina are removed; the insoluble sodium titanate is brought into solution by treatment with potassium bisulphate, and the titanium dioxide precipitated from an acetic acid solution as described by Gooch. The crucial point is the insolubility of the phosphotitanate of iron in dilute hydrochloric acid, and neither of the authors specify the strength of the acid to be employed. In the descriptions which follow, the words "per cent." denote the parts by weight of anhydrous hydrochloric acid per 100 grams of solution.

The experiments were carried out in the following manner: A portion of the standard titanium dioxide solution was taken, and 0.5 gram iron as $Fe_2(SO_4)_3$ added; the hydroxides, precipitated by ammonia and a slight excess of acetic acid, were washed and dissolved in hydrochloric acid, and, after the addition of 1 gram of ammonium phosphate, the solution was evaporated to dryness and baked at the highest temperature of the hot plate for seven hours. To ascertain approximately the temperature to which the material was exposed, a thermometer was placed in an empty beaker on the same spot on the hot plate and left for some hours; the highest temperature reached was 180° C. The cooled mass was then digested with 0.4 per cent. hydrochloric acid for some hours at a temperature of about 100° C., but no action of any

[1] Blair's "Analysis of Iron and Steel," 4th edition, p. 85.
[2] Morgan: *Chemical News*, **75**, 134.
[3] Arnold: "Steel Works Analysis," p. 195.
[4] Waterhouse: *Chem. News*, **85**, 198.

consequence ensued. With 2 per cent. hydrochloric acid, the hard mass softened and loosened from the bottom of the beaker after a short digestion; it was filtered off, washed, and the titanium dioxide in the filtrate estimated.

	Weight of solution. Grams.	TiO_2 taken. Gram.	TiO_2 in filtrate. Gram.
(19).....	11.181	0.1052	0.0020
(20).....	11.158	0.1051	0.0025

The residue containing the phosphotitanate still retained a large quantity of basic ferric salts, and, on following out the method of analysis as given, the final precipitation of the titanium dioxide had to be made in the presence of a considerable quantity of iron reduced to ferrous condition by sulphur dioxide. It is well known that unless the amount of iron be small, the separation under these circumstances is incomplete and in this experiment both of the precipitates of titanium dioxide were markedly contaminated with ferric oxide. To acquire further information, the experiment was repeated with slight modifications. The same quantities of titanium dioxide and ferric sulphate were taken; the baking lasted six hours; the mass was then digested with 50 cc. of 2 per cent. hydrochloric acid for two hours and finally boiled for half an hour. After filtering, estimations of the iron and titanium in the filtrate were made; the insoluble residue was returned to the beaker, 50 cc. of 4 per cent. hydrochloric acid added, and digestion carried on for fifteen hours at a temperature of 60° C. The solution was again filtered and the iron and titanium estimated in the filtrate.

	TiO_2 extracted.	Total TiO_2 extracted.	Fe extracted.	Total Fe extracted.
Two per cent. HCl (21).....	0.0048	.....	0.1700	.....
(22).....	0.0022	.....	0.1140	.....
Four per cent. HCl (21).....	0.0040	0.0088	0.1373	0.3073
(22).....	0.0037	0.0059	0.1151	0.2291
Taken: TiO_2 = 0.1050 gram.		Fe = 0.5000 gram.		

Taking mean values, 2 per cent. hydrochloric acid extracted 28 per cent. of the iron present and 3.5 per cent. of the titanium dioxide; 4 per cent. hydrochloric acid extracted 54.6 per cent. of the iron and 7 per cent. of the titanium dioxide.

A third trial was made with a titaniferous magnetite containing 44 per cent. of iron and 13 per cent. of the titanium dioxide. To 1 gram of the ore in impalpable powder were added

1 gram ammonium phosphate and 20 cc. of concentrated hydrochloric acid, and digestion at a temperature of nearly 100° C. was carried on for seven hours. The solution was evaporated to dryness, baked for five hours, digested with 2 per cent. hydrochloric acid for half a day and finally boiled for a short time. The same process was repeated with portions of the same acid of greater strength.

		TiO_2 extracted.	Total TiO_2 extracted.	Fe extracted.	Total Fe extracted.
Two per cent. HCl	(23)...	0.0043	....	0.2069	....
	(24)...	0.0054	....	0.2175	....
Four per cent. HCl	(23)...	0.0036	0.0070	0.1510	0.3579
	(24)...	0.0048	0.0102	0.1288	0.3463
Six per cent. HCl	(23)...	0.0085	0.0164	0.0483	0.4062
	(24)...	0.0080	0.0182	0.0506	0.3969

Quantities present in sample: $TiO_2 = 0.130$ gram; $Fe = 0.440$ gram.

Taking mean values we get:

	2 per cent. HCl. Per cent.	4 per cent. HCl. Per cent.	6 per cent. HCl. Per cent.
TiO_2 extracted	4	7	13
Fe extracted	48	80	91

The serious inaccuracies to which the process is subject nullify its value as a method of separation, and only the possibility of its employment as a rapid, approximate method for technical work remains.

For such a purpose the following points should be noted. The baking should be thorough but not necessarily long; probably an hour at about 200° C. is sufficient. Four per cent. hydrochloric acid should be used for the extraction of the iron, boiling until solvent action apparently ceases; if there remain a considerable quantity of reddish ferric salts, the strength of the hydrochloric acid may be raised to 6 per cent., which should on boiling almost complete the extraction. If 4 per cent. acid has been used, the probable loss in the titanium dioxide will be from 5 to 10 per cent., with 6 per cent. hydrochloric acid, from 10 to 15 per cent.

HILGER AND HAAS' METHOD.

While studying the separation of titanium and tin, Hilger and Haas[1] discovered that by igniting the mixed oxides in hydrogen and then boiling with dilute sulphuric or hydrochloric acid, the reduced tin could be dissolved without apparent loss in titanium. The method was also applied to the separation of titanium and

[1] Hilger and Haas: *Ber. d. chem. Ges.*, **23**, 458.

iron, but no analytical results could be found in any of the literature to which the writer had access. For the analysis of ores and minerals the following process is recommended by the authors. The finely ground material is treated with sulphuric and hydrofluoric acids; after the removal of the silica, the latter acid is expelled by evaporation and the solution is transferred to a casserole, neutralized with potassium hydroxide, 2 grams sulphuric acid added, and the volume made up to 400 cc. The liquid is then boiled for six hours, the bulk being kept constant by adding water and the precipitated titanium dioxide filtered off; the acidity of the filtrate is again adjusted to 0.5 gram sulphuric acid per 100 cc., and a further boiling is carried on to recover any titanium which may still remain in solution. The total precipitate, which contains all the tin and a small quantity of iron, is then reduced in hydrogen for from fifteen to thirty minutes and boiled gently with 20 per cent. hydrochloric acid for half an hour. , Tin and iron are dissolved, the titanium dioxide is filtered off, and, unless the amounts are small, the reduction and extraction are repeated.

Ledebur[1] has described a modification of the process suitable for iron ores. The ore is reduced in hydrogen, boiled with dilute sulphuric acid 1 : 40, and the insoluble residue filtered off, treated with hydrofluoric acid, dried, fused with sodium carbonate, leached, re-fused with potassium bisulphate and the melt dissolved in water. The titanium dioxide is then precipitated by boiling for an hour at a bulk of 450 cc.; no precautions for regulating the acidity of the solution are stated.

The important point is evidently the insolubility of the titanium dioxide, either as it occurs naturally or in the form of metatitanic acid; some experiments covering this question were, therefore, made. For convenience, an iron ore was first tested according to Ledebur's directions, as given above. One gram of a titaniferous magnetic was reduced at a red heat in hydrogen for an hour and boiled in dilute sulphuric acid, 1 : 40, for twenty minutes, the evolution of hydrogen ceasing after about ten minutes. Estimations were then made in the filtrate by color. In one experiment there was found 5 milligrams titanium dioxide, in another 5.2 milligrams. These would cause losses of 4 per cent. in the titanium dioxide found.

[1] Ledebur: Leitfaden f. Eisen. Lab., 5th edition, p. 38.

In another case the same ore was reduced in hydrogen at a perceptibly higher temperature for two hours, and the filtrates tested after boiling in dilute sulphuric acid of the same strength. In one there remained 3.6 milligrams titanium dioxide, in the duplicate 4 milligrams; these correspond to losses of 3 per cent. in the titanium dioxide present.

To get an idea of the total losses which might occur in proceeding according to Hilger and Haas' directions, the following experiment was tried: To a weighed quantity of the standard titanium solution was added 0.5 gram iron as $FeSO_4$, and the acidity regulated to 0.5 gram sulphuric acid per 100 cc., as described. The solutions were boiled at a volume of 400 cc. for six hours with the addition of water as required, the precipitate was filtered off and the filtrates, after a renewed adjustment of the acidity, were subjected to a further boiling for two hours. The slight additional precipitate was added to that already collected, the whole dried and, after reduction in hydrogen for an hour and boiling for a short time with dilute sulphuric acid 1 : 40, the titanium dioxide was filtered off, ignited and weighed.

	Weight of solution. Grams.	TiO_2 by standard. Gram.	TiO_2 found. Gram.	Fe_2O_3 therein. Gram.	TiO_2 found. less Fe_2O_3. Gram.	Error.
(25) ..	11.142	0.1049	0.1008	0.0009	0.0999	0.0050—
(26) ..	11.130	0.1049	0.1088	0.0145	0.0943	0.0106—
(27) ..	11.113	0.1047	0.0888	0.0004	0.0884	0.0163—
(28) ..	11.122	0.1048	0.1017	0.0011	0.1006	0.0042—

The results in (25) and (28) agree with those obtained previously in the case of the ore, but (26) and (27) show a wide variation; no reason can be assigned for this behavior for (25) and (26) were carried out together and afterwards the other pair in like manner. The precipitation from the sulphuric acid solution was, in all cases, practically complete, as was shown by colorimetric estimations in the filtrates, while the same method revealed the fact that exceptionally large amounts were dissolved by the dilute sulphuric acid 1 : 40, in numbers (26) and (27). It would have been interesting to have had the record of some further experiments to enable one to judge whether the heavy losses were extraordinary or not, but the best results already obtained were not very promising as regards accuracy, and other matters were more urgent. If we except numbers (26) and (27) —although there is no justification for this except the largeness

of the error—the method will be seen to offer a slightly greater accuracy than Arnold's with a very convenient feature in the shape of the almost complete removal of the iron in the initial stage, without the heavy losses in titanium which accompany a treatment of phosphotitanate of iron with hydrochloric acid of a strength greater than 2 per cent. Even in Hilger and Haas,[1] published work, among six results of separation of titanium from tin, three are subject to negative errors of 5.6, 6.3 and 7.5 per cent. in the amount of titanium dioxide found; such deficiencies are only negligible in dealing, as was the case in this instance, with small quantities of the element under discussion.

For the precipitation of titanium, Hilger and Haas make use of the directions given by Lévy,[2] who has made an extensive study of some of the compounds of this element. In the course of the investigation, it was found necessary to test the analytical methods, and the discovery was made that titanium was completely precipitated on boiling a solution of its sulphate which contained 0.5 gram sulphuric acid per 100 cc.; in the presence of the alkalies, magnesium, zinc, copper, and even aluminum the separation was found to be complete. An instructive table is given by Lévy, which is reproduced below as an example of the manner in which the precipitation of titanium dioxide is influenced by the amount of free acid present. Portions of a solution of pure titanium sulphate were partially neutralized with potassium hydroxide and boiled for six hours at constant volume.

No.	Vol. of liquor. cc.	Total H_2SO_4. Grams.	Free H_2SO_4. Grams.	TiO_2 found. Gram.	TiO_2 taken. Gram.	
(1)	100	3.561	1.0	0.082	0.086	
(2)	100	3.561	0.5	0.085	0.086	
(3)	100	3.561	0.0	0.100	0.086	
(4)	100	3.561	0.0	0.108	0.086	(excess of KOH)
(5)	150	5.766	5.766	0.000	0.036	
(6)	150	5.766	0.983	0.036	0.036	
(7)	150	5.766	0.000	0.047	0.036	

Lévy makes the statement that "In acetic acid, titanium dioxide is partially precipitated even in the cold, but never completely on boiling." No particulars of any experiments are given, but one wonders how he arrived at any such conclusion.

OTHER RECENTLY PROPOSED METHODS.

As has been intimated previously, the methods which have

[1] Hilger and Haas: *Loc. cit.*

[2] Lévy: Ann. chim. phys. [6], **25**, 433.

already been discussed were chosen because of the economy of time which they appeared to offer; of the other processes or modifications recently proposed which have come under the writer's notice, none appear to be free from objection, either on account of inaccuracy or of the amount of time required for their operation.

When in search of rapid methods one turns first to volumetric analysis, but unfortunately in that direction no accurate process for the estimation of titanium is available. Wiegand[1] has studied the volumetric method proposed by Pisani[2] and, with all the improvements which could be devised, found it still unsatisfactory. In the presence of titanium and iron the solution was reduced with zinc until the color no longer changed, then potassium permanganate was slowly added till a drop gave a red coloration with potassium thiocyanate. Errors of 3 to 4 per cent. are numerous among the results given; even with portions of a pure solution of titanium sulphate which were reduced and reoxidized, the errors in determination averaged 3.7 per cent. Wells and Mitchell,[3] investigating the same method, proceeded upon a slightly different plan. Two equal quantities of a solution containing iron and titanium were taken, one was reduced with hydrogen sulphide, the other with zinc, the titanium being estimated by difference. Even with elaborate precautions, no better results were obtained. In ten determinations published, the lowest error was 2 per cent. and the highest 6 per cent.

Walker[4] has founded a method of separation from iron upon the observation that salts of titanium oxidized with hydrogen peroxide are not immediately precipitated by ammonia. An excess of the former reagent is added to the solution containing the two elements as sulphates and the whole is allowed to flow gently into ammoniacal hydrogen peroxide. Three separations were found to be necessary to separate 0.1 gram iron from the same amount of titanium dioxide; the results are excellent, but the number of operations appear to be a drawback.

In Rothe's[5] method, which has found such extended use for the separation of nickel and iron, titanium, if present, remains

[1] Wiegand: *Ztschr. anal. Chem.*, **21**, 510.
[2] Pisani: *Compt. Rend.*, **59**, 289.
[3] Wells and Mitchell: This Journal, **17**, 878.
[4] Walker: This Journal, **20**, 513.
[5] Rothe: *Mitth. König. Tech. Vers. Anst.*, Berlin, 1892, Part III.

in the acid solution and is therefore separated from iron; no analytical data are available, however, for guidance in forming an opinion.

Mathews[1] has described as a means of separating iron from titanium, zirconium, and some of the rare earths, a modification of Rothe's method. The mixed, dried chlorides of the elements are heated with absolute ether and dry hydrochloric acid gas; the ferric chloride dissolves, leaving as a residue the chlorides of the other element or elements.

Although not at present very promising from the standpoint of speed, the three methods last described have interesting possibilities and deserve investigation; unfortunately, the time for a study of their efficiency has hitherto been lacking, but it is hoped that some experiments in this direction will shortly be carried out.

As a result of the study which has been made, it has been found that Baskerville's method is superior in accuracy to either of the others, but the writer is of the opinion that the modification of Gooch's method, described by Blair, is the best which has yet been made public. An excellent and detailed description of this process is given by Pope;[2] it does not take more time to carry out than does Baskerville's, and in the hands of the writer, has proved the more accurate.

FACULTY OF APPLIED SCIENCE,
UNIVERSITY OF TORONTO. July, 1903.

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

REDUCTION OF 2,5-DIMETHYLBENZALDAZINE AND THE PREPARATION OF SOME OF ITS SALTS.

BY EVERHART PERCY HARDING AND LILLIAN COHEN.

Received July 25, 1903.

Preparation of the Hydrochloride of 2,5-Dimethyldibenzylamine.[3]

$$(CH_3)_2C_6H_3.CH_2\rangle NH.HCl.—$$
$$(CH_3)_2C_6H_3.CH_2\rangle$$

—From 2 to 5 grams of 2,5-dimethylbenzaldazine, prepared

[1] Mathews: This Journal, **20**, 846.

[2] Pope: *Trans. Am. Inst. Min. Eng.*, **29**, 372.

[3] The free base—dimethyldibenzylamine has not yet been analyzed.

according to the method of Curtius and Jay[1] from 2,5-dimethylbenzaldehyde, prepared by the Gatterman-Koch method,[2] were dissolved in 95 per cent. alcohol, some glacial acetic acid, and an excess of zinc dust added, and the flask with reflux condenser placed upon a water-bath, and the mixture gently boiled for about four hours. Upon the addition of very dilute sulphuric acid the unchanged azine was filtered off and to the filtrate, made strongly alkaline with sodium hydroxide, was added dilute hydrochloric acid. Upon standing some time, the hydrochloride crystallized out in the form of white, satin-like needles which crystallized from dilute alcohol in the form of colorless, prismatic needles and which melted at 227°. An analysis showed the following percentage composition:

	Calculated. Per cent.	Found. Per cent.
Carbon	74.74	74.70
Hydrogen	8.30	8.48
Nitrogen	4.84	4.91
Chlorine	12.11	12.10

2,5-Dimethyldibenzylaminehydrochloride is very soluble in ethyl and methyl alcohols and benzene, and slightly soluble in acetone. It is insoluble in cold but soluble in hot water.

2,5-Dimethyldibenzylamine Nitrate, $C_{18}H_{22}N.HNO_3$.—The nitrate was prepared by adding sodium hydroxide to a water solution of the hydrochloride and then treating the solution with dilute nitric acid. The nitrate precipitated at once as a white, crystalline substance which recrystallized out of dilute alcohol in the form of thin, colorless plates of the monoclinic system which melted at 215°. The analysis gave 8.86 per cent. N. Calculated, 8.80 per cent.

The nitrate is soluble in ethyl and methyl alcohols and insoluble in benzene. It is very difficultly soluble in acetone. It is soluble in hot, but insoluble in cold water.

2,5-Dimethyldibenzylamine Picrate, $C_{18}H_{23}N.C_6H_2(NO_2)_3OH$. —The picric acid derivative was prepared by adding to a concentrated alcoholic solution of the free base a concentrated alcoholic solution of the calculated amount of picric acid. The picrate was then precipitated by adding water. The voluminous precipitate was then filtered off, washed well with water and crystallized out of dilute alcohol. Upon crystallizing several times out of alcohol, the short sulphur-yellow prisms melted at 142°.

[1] *J. prakt. Chem.*, Neue Folge, **89**, 43.
[2] *Ber. d. chem. Ges.*, **30**, 1622.

The picrate is soluble in ethyl and methyl alcohols and very soluble in benzene and acetone. It is slightly soluble in hot but insoluble in cold water.

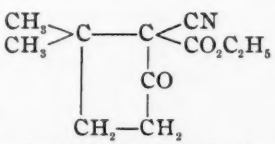
2,5-Dimethyldibenzylamine Mercuric Chloride, $(C_{18}H_{23}N.HCl)_2HgCl_2$.—A concentrated water solution of mercuric chloride was added to a concentrated water solution of the hydrochloride. Upon standing, a white precipitate crystallized out which, upon recrystallizing out of alcohol, crystallized in long, colorless prisms which melted at 157.5°. The crystals are very soluble in ethyl and methyl alcohols and less soluble in benzene. They are very soluble in warm and slightly soluble in cold water.

2,5-Dimethyldibenzylamine Chlorplatinate, $(C_{18}H_{23}HCl)_2.PtCl_4$.—The platinum double salt was prepared by adding to a concentrated water solution of the hydrochloride a concentrated solution of chlorplatinic acid. The salt soon precipitated which recrystallized from alcohol in the form of reddish yellow, prismatic needles which melted at 188°. An analysis gave 21.22 per cent. of platinum, calculated 21.01 per cent. The double salt is soluble in ethyl and methyl alcohols and in acetone. It is insoluble in benzene and in hot and cold water.

SYNTHESIS OF β-METHYLADIPIC ACID.[1]

By William A. Noyes and Irving J. Cox.

Some time ago[2] one of us found that dimethylcyancarboxethylcyclopentanone,



is decomposed by sodium hydroxide with formation of the sodium salts of malonic and hydroxyisocaproic acids. So far as we are aware, no other similar elimination of a carbon atom, by saponification, from a cyclic compound has been observed, and it seemed of interest to determine whether the reaction is a general one. To throw further light on this question, we have attempted to

[1] The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute.

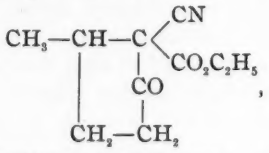
[2] This Journal, **23**, 396.

prepare a similar compound containing one methyl group instead of the two. The amount of the desired compound formed was too small for our original purpose, but some new compounds which seem worthy of a brief description were obtained.

Reduction of Levulinic Acid.—The levulinic acid was prepared from sugar and was purified by one distillation under diminished pressure.[1] From 75 to 80 grams of the acid were obtained from 500 grams of sugar.

For reduction, the acid was divided into portions of 10 grams each, and each portion dissolved in 25 cc. of water. About 225 grams of 3 per cent. sodium amalgam were added slowly to each portion, excessive heating being avoided. After standing for thirty-six hours, the different portions were united, acidified with sulphuric acid, 1 : 1 by volume, and the valerolactone distilled in a current of steam. The distillate was boiled with enough sodium hydroxide to make it alkaline and the solution evaporated nearly to dryness. The residue was acidified, the solution extracted with ether, and, after drying with sodium sulphate and distilling off the ether, the lactone was distilled under atmospheric pressure. Fifty-one grams of the lactone were obtained from 81 grams of the acid. The method is similar to that of Neugebauer,[2] but differs in detail and, especially, in that Neugebauer took fourteen days for the reduction. Our yield was also a little better.

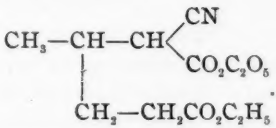
Condensation of γ-Chlorvaleric Ester and of γ-Bromvaleric Ester with Cyanacetic Ester.—γ-Chlorvaleric ester was prepared by treating the lactone with absolute alcohol and hydrochloric acid. By condensing the chlorester with cyanacetic ester by means of sodium ethylate[3] and distilling the resulting products under diminished pressure, a small amount of a crystalline product, which melted at 185°, was obtained from the portion which came over last. It is believed that this compound was 2-methyl-1,1-cyancarboxethylcyclopentanone,



[1] Noyes' "Organic Chemistry for the Laboratory," p. 67.
[2] *Ann. Chem.* (Liebig), **227**, 100.
[3] This Journal, **23**, 397.

but the amount obtained was too small for analysis or for further examination.

β-Methyl-α-cyanadipic Ester,

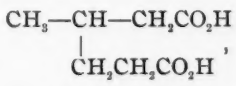


—When γ-bromvaleric ester is condensed with cyanacetic ester, methylcyanadipic ester was formed instead of the cyclic compound, which was desired. This boils at 175°-185° under a pressure of 20 mm. The yield was much greater than with the chlorester. The analysis gave: C, 60.29, 60.09; H, 7.97, 7.99; N, 5.96. Calculated for C, 59.75; H, 7.83; N, 5.81.

3-Methylhexanoic-1,2',6- Acid.—By saponifying with alcoholic sodium hydroxide, evaporating, dissolving in water, acidifying and extracting with ether, the corresponding tribasic acid was obtained. On slow evaporation of its aqueous solution, the acid crystallizes in plates which melt and decompose at 127°-128°.

The Calcium Salt, $(C_8H_9O_6)_2Ca_3 + 3H_2O$, is sparingly soluble in water. The analysis gave: Ca, 20.92, 20.63; H_2O at 200°, 9.20, 9.36. Calculated for Ca, 20.83; H_2O, 9.37.

β-Methyl Adipic Acid,

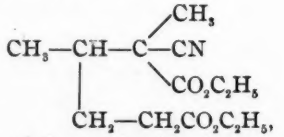


if formed when the tribasic acid is heated for a short time to 200°. After crystallization from benzene, the acid melted at 89.2°. On titration with lime-water, 0.0632 gram required the equivalent of 7.73 cc. N/10 alkali. Theory requires 7.90 cc. In a second experiment, 0.0315 took 3.86 cc.; calculated, 3.94 cc.

The melting-point of *active* β-methyladipic acid is given by Manasse and Rupe[1] as 88.5°-89°; by Baeyer[2] as 89°; by Semmler[3] as 84.5°; and by Wagner[4] as 93°-94.5°.

[1] *Ber. d. chem. Ges.*, **27**, 1820.
[2] *Ibid.*, **29**, 30.
[3] *Ibid.*, **25**, 3516.
[4] *Ibid.*, **27**, 1642.

2,3-Dimethyl-2-cyanadipic Ester,



was prepared, as usual, by condensing the monomethyl ester with methyl iodide by means of sodium ethylate in an alcoholic solution. It boils at 181°-194° under a pressure of 29 mm.

The analysis gave:

Calculated for $C_{13}H_{21}O_4N$, C, 61.18; H, 8.24; N, 5.49. Found: C, 61.12, 61.95; H, 8.49, 8.53; N, 5.43.

2,3-Dimethyl-1,2',6 Acid.—The ester was saponified with much greater difficulty than the corresponding monomethyl ester. It required two days' heating on the water-bath with sodium hydroxide before the evolution of ammonia was complete. The resulting tribasic acid crystallizes in pearly white granules which melt at 159°. On titration with lime-water, 0.0361 gram took the equivalent of 5.07 cc. N/10 alkali, and 0.0407 gram took 5.55 cc.; calculated, 4.97 cc. and 5.60 cc.

α,β-Dimethyladipic Acid.—The dimethyladipic acid, formed by heating the tribasic acid to 200°, could not be induced to crystallize. An analysis of its silver salt gave 55.45 per cent. silver; calculated for $C_8H_{12}O_4Ag_2$, 55.67 per cent.

The copper salt from another preparation gave only 24.90 and 24.98 per cent. copper instead of 27.00 per cent calculated. A salt containing 1 molecule of water would give 24.68 per cent. of copper, and it seems probable that this was the composition of the salt, but such evidence is not altogether satisfactory. We had no time for the further investigation of the salt.

NOTES.

Note on the Avery-Beans Method for the Determination of Arsenious Acid in Paris Green.—This method rests on the principle that arsenious acid may be titrated with iodine in the presence of cupric salts, provided an alkaline tartrate be present. As originally published,[1] the method gives accurate results only when

[1] This Journal, **23**, 485.

no free, white arsenic appears on treating the green with cold dilute hydrochloric acid. In this laboratory I have, for some time, treated such greens as show a tendency to separate out white arsenic as follows: The sample is treated with hydrochloric acid (approximately 0.5 N) solution and boiled gently. Five to 10 cc. of acid for each 0.1 gram of green is sufficient. No loss of arsenic by volatilization takes place unless the solution becomes concentrated to less than one-half its original volume. If solution is not effected, add a cold saturated solution of sodium acetate, using about 3 grams of the salt for each 0.1 gram of the green originally weighed out, and boil till all arsenious acid dissolves. The dilute acid dissolves all copper and what we may call "firmly combined white arsenic." The concentrated acetate solution dissolves all white arsenic left by the acid. The proportions of the two solvents may be varied to meet the requirements of individual greens, but all copper should be in solution before the acetate is added. After solution is effected, an alkaline tartrate and solid bicarbonate are added and the diluted solution titrated as usual.

LINCOLN, NEB., Sept. 1, 1903. S. AVERY.

NEW BOOKS.

ANALYTICAL CHEMISTRY. Vol. I. QUALITATIVE ANALYSIS. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic of Zurich. Translated from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. New York : John Wiley and Sons. 1903. Price, $3.00.

This book is an amplified reproduction of the lectures on qualitative analysis that Professor Treadwell has delivered yearly at Zurich since 1882. The first German edition was issued in 1899 and met with such a favorable reception that it was followed two years later by a second edition which now appears in English form.

The general plan is that usually followed in text-books on this subject. Under the heading General Principles, an introduction of some thirty pages treats briefly of precipitation, oxidation and reduction, hydrolysis, mass action and the ion theory. The last two subjects are alluded to occasionally in the body of the text but are not made the basis of the method of presentation.

The chief feature of the work is the treatment of the action of the various reagents on solutions of pure salts. Explanations of the mechanism of these reactions are introduced in detail, in connection with which free use is made of equations and graphical formulas. The result is a valuable work for ready reference, especially valuable in that it embodies the ideas of a chemist of twenty years' experience in teaching the subject.

The book is an expansion of the old style text-book on the subject and its chief faults are inherent in the method of presentation. It is to be regretted that, with the exception of the pages in the introduction giving directions for the determination of the sensitiveness of reactions, there is scarcely a hint in the whole book that the majority of reactions cannot be represented quantitatively by an equation unless the conditions as to the temperature, concentration, etc., are allowed to vary only within relatively narrow limits. An occasional lack of conservatism of statement about reactions which are complicated and uncertain, or vary under slightly varying conditions, is also unfortunate. The impression is conveyed that such reactions have actually been proved to take place in the way explained and often a distinction is not drawn sharply enough between what is known to happen and what is supposed to happen. For example we find such statements as the following: "The oxidizing action of nitric acid depends upon the formation of the anhydride which then breaks down into nitric oxide and oxygen," page 4; "if an excess of hydrogen peroxide is used" in oxidizing chromic acid to chromium peroxide "a lively evolution of oxygen will ensue; the chromium peroxide as well as the hydrogen peroxide will be reduced. The oxygen comes from the hydrogen peroxide while the hydrogen of the latter is oxidized by the chromium peroxide to water," page 85.

These faults are especially noticeable in the supplement which treats of the rarer metals. Much of the matter here given has no place in a book of this sort. The reactions of the "pure" salts of these elements are of interest, if it is actually known what these reactions are; but a treatise on Qualitative Analysis which gives the impression to the student that the behavior of the rare elements is as definitely and exactly known as that of iron, and which, aside from a table giving a method of analysis for gadolinite, ignores the separation of these elements from the commoner ones, might better leave the whole field of the rarer elements untouched. We

note that "there are no characteristic dry reactions" of Thorium, page 16. Of the nine wet reactions enumerated, not one is characteristic. The only characteristic reaction of the element, that with a solution of potassium trinitride[1] containing hydronitric acid, is not mentioned. Under neodymium and praseodymium we find the statement "it is very difficult to separate these two metals from one another. It is accomplished only by repeated fractional crystallization of the ammonium double nitrate." The fact that the presence of another base, such as lanthanum, makes this separation possible in comparatively few crystallizations is not mentioned.

The proof-reading leaves something to be desired; but in a book that contains as many formulas and equations as this, an occasional error is almost unavoidable. That a few typographical errors in the first German edition should have survived not only the second edition in that tongue but a translation as well, is, however, surprising. Such errors appear in equations on pages 157 and 206. Of other errors may be cited the precipitation of cobalt by potassium nitrate, page 143, and the use of nitric for hydrochloric acid on page 235, line 9. In general, the methods used in the separation and detection of the elements have been well chosen. Hillebrand's method for the detection of the vanadium is introduced in this edition. The only seriously faulty method which strikes the eye is that for the detection of hydrochloric acid in the presence of hydrobromic and hydriodic acids. This is attempted by fractional precipitation of the silver salts until finally a white precipitate is produced. The adoption of a test of this sort is inexcusable when we have at our command the excellent separations based on the oxidation of hydrobromic and hydriodic acids by appropriate oxidizing agents.[2]

The plate of the spectra is very poor, but the typography and press work of the book are good, and the translation has been well done.

THEODORE WHITTLESEY.

RADIUM AND OTHER RADIO-ACTIVE SUBSTANCES, ETC. By WILLIAM J. HAMMER, Consulting Electrical Engineer. New York: D. Van Nostrand Company. Price, $1.00.

This booklet of 72 pages represents a lecture delivered before a joint meeting of the American Institute of Electrical Engineers

[1] L. M. Dennis: This Journal, **18**, 947.

[2] See Hart: *Am. Chem. J.*, **6**, 346; Benedict and Snell: This Journal, **23**, 809.

and the American Electrochemical Society. The section devoted to radium and radio-active bodies is very instructive and exceedingly entertaining. In the letter to the author, M. Curie writes, "Where is the source of this energy? Both Mme. Curie and myself are not able to go beyond hypotheses. One of these consists in supposing the atoms of radium evolving and transforming into another simple body and, despite the extreme slowness of that transformation, which cannot be located during a year, the amount of energy involved in that transformation is tremendous."

Every chemist will find in the various paragraphs in this book much material for reflection. Having studied the data here submitted and read Barker's most interesting fasciculus entitled "Radio-activity and Chemistry," he will have had brought to him a very complete and accurate account of the marvelous results which have been noticed in recent years, along lines which he probably never dreamed could include his beloved and simple atom. It is said the lamented Rowland once remarked, "that a Steinway grand piano was a comparatively simple piece of mechanism compared with an iron atom." It would indeed seem after perusing the pages of Mr. Hammer's book, as if not only the iron atom, but the atoms of many more of our elements were not only complex, but were undergoing a subtle and constant change.

The second section of Mr. Hammer's book gives in a very succinct form most interesting accounts of the properties and application of selenium, while in the third section there is presented briefly, it is true, but at the same time most interestingly, an account of the treatment of diseases by ultra-violet rays. It is here that a description of the Finsen Institute at Copenhagen is given with a description of the treatment of Lupus vulgaris.

This publication deserves to be widely read because of the new facts which it presents and because of its suggestiveness. Certain typographical errors appear, but these will no doubt be corrected in a subsequent edition of the book. EDGAR F. SMITH.

DIE CONSTITUTION DES KAMPHERS UND SEINER WICHTIGSTEN DERIVATE, VON OSSIAN ASCHAN. Braunschweig: Friedrich Vieweg und Sohn. 1903. pp. xi + 117.

So many workers have busied themselves with the subject of camphor, and the material accumulated has become so com-

plicated, that such a book as the present one is very welcome. Without attempting to give any details as to physical properties or methods of preparation for the derivatives of camphor, it does give a very clear oversight of nearly all of the relationships among those compounds which are important in establishing its structure. The work includes: 1, A brief statement with regard to each of the thirty-three formulas which have been proposed for camphor (or for camphoric acid); 2, a summary of the facts which must be considered in deciding what is the true structure; 3, a criticism of the formulas which have been proposed. This criticism demonstrates, conclusively, that of all the formulas proposed Bredt's is the only one which can now be considered as possible; 4, a consideration of other important decomposition products of the camphor; 5, a discussion of the structure of camphene and borylene.

When we consider the very large number of compounds which must be spoken of in such a discussion and the confusion which exists in the nomenclature of some of these bodies, it would seem almost impossible to avoid some mistakes. Very few have been noticed. The most important are the following: On page 61, α-dihydrohyhroxy-β-campholytic acid is spoken of as identical with [γ]-dihydrohydroxy-α-campholytic acid; on page 57, Walker's "allocampholytic acid" is called "α-campholytic acid"; and on page 68, the active α-campholytic acid is not properly distinguished from the racemic form of the same compound.

The student who is interested in the special study of camphor will find the book a most useful summary of our present knowledge of the subject, and the general student can scarcely find a better illustration of the nature of the work which must be done for the determination of the structure of a complex organic compound. And the fact that the solution of the problem which has been reached has the support of every one familiar with this particular field, in spite of the diversity of opinion which has prevailed till very recently, demonstrates that very positive results have finally been obtained. W. A. NOYES.

L'ACÉTYLÈNE. THÉORIE. APPLICATIONS. BY MARIE-AUGUSTE MOREL. Paris: Libraire Gauthier-Villars. 1903. 8 vo. xii + 169 pp.

This book is written by an engineer and gives a thermochemical and mathematical treatment of its subject. Its contents are well

indicated by the chapter headings: I, General remarks upon the constitution of the hydrocarbons; II, general remarks upon the metallic carbides and the generation of the hydrocarbons; III, calcium carbide, its physical and chemical properties, its aplications; IV, acetylene, its preparation, its physical, chemical, and toxic properties; V, the calorific, optical, and explosive properties of acetylene. Burners: VI, The different applications of acetylene. Lighting, heating, motive force: VII, New considerations upon generating apparatus for acetylene gas. A note upon the thermodynamic potential is appended. The sixth chapter begins with a brief history of artificial illumination in general.

There are a few noticeable errors. On page 33 an equation is balanced, using the formula CaCl for calcium chloride. On pages 40 and 54 no attention has been paid to the work of Keiser,[1] who has shown that cuprous acetylide contains no oxygen and no hydrogen. The author gives it the formula C_2HCu_2OH on page 40. Dr. Auer von Welsbach's name is spelled "Velbasch" on page 101. On page 150, a figure is given to parts of which reference is made in the text by letters, none of which appear in the figure. Some of these may be the fault of the printer.

The book is very well written, although the author occasionally lapses into poetical expressions. He is, perhaps, ultra-enthusiastic in favor of the use of acetylene for lighting anything or any place, but all his comparisons are made fairly and do not deal in generalities.

Very little apparatus is described, but the author says in his preface that he intends to describe only that which is most nearly correct theoretically.

The typographical work is generally good.

The book is of value to engineers and others who are interested in the installation of apparatus for the production of acetylene. It is also a useful addition to the library, for it gives a condensed and systematic form, quite a complete résumé of the chemistry and uses of acetylene.

BENTON DALES.

[1] *Am. Chem. J.*, **14**, 285.